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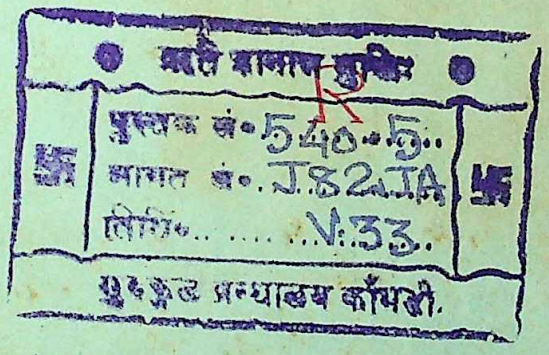
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4788

Issued with the January Number, 1911.

Proceedings.

COUNCIL.

A letter ballot was sent to the Council on October 11th in which President Bancroft requested authority from the Council to appoint a committee to investigate the whole question of the Industrial Journal and make any recommendations they saw fit to the Council at or before the annual meeting in Minneapolis. The vote was counted on November 1st and the authority asked for was granted. President Bancroft has appointed the following committee: A. D. Little, *Chairman;* L. H. Baekeland, W. D. Bigelow, Wm. Brady, W. C. Geer, T. J. Parker and W. R. Whitney.

On November 3rd a second motion, made by W. R. Smith, was sent to the Council, moving reconsideration of the previous motion. The ballot for reconsideration was counted on November 25th and was found not to have passed.

On November 11th a letter ballot was sent to the Council carrying the following resolution; namely:

"WHEREAS, The number of members of the American Chemical Society in the State of Michigan has increased so that it has become desirable to restrict the territory of the present section, to the end that other local sections may be formed in Michigan when desirable, therefore be it

"*Resolved,* (1) That the Council of the American Chemical Society is hereby requested to amend the charter granted on December 7, 1899, so that the territory to be embraced by this section shall be restricted to that portion of the State of Michigan within a radius of ten miles from the headquarters at the University of Michigan. (2) That the Council is requested to designate this section in the future as the University of Michigan Section."

This ballot was counted on December 2nd and was found to have passed the Council. The University of Michigan Section has, accordingly, been informed of the amendment of the original charter.

On the same date as the above-mentioned ballot, owing to the peculiarities of train service to Minneapolis, it was moved that the time of holding the Council meeting at Minneapolis be left to the President and the Secretary with power. This ballot was also counted on December 2nd and was found to have unanimously passed the Council.

President Bancroft has appointed the following to represent the American Chemical Society in determining the Perkin Medal award: M. C. Whitaker, *Chairman;* G. P. Adamson, H. R. Carveth, Henry Howard, J. A. Mathews, J. Merritt Matthews.

CHARLES L. PARSONS,
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BOARD OF DIRECTORS.

The Directors of the American Chemical Society met at the Chemists' Club at 5 P.M., Saturday, December 3rd, with all of the directors present.

It was voted that the contract with the advertising agent be so modified that Mr. Mack be guaranteed continuation in office until October 1, 1912, provided he shows due diligence in the prosecution of the Society's advertising business.

It was voted that advertising agencies be allowed a discount of not exceeding 10 per cent.

It was voted that the secretary be directed to write again to W. D. Richardson regarding advertising contracts and to ask him to transmit to the secretary on or before December 15th a list of all amounts due the Society on advertising secured by him and that Mr. Harvey F. Mack be directed to collect all such bills not paid before December 31, 1910, and be allowed 5 per cent. commission for such collection.

It was voted to transfer $150.00 from incidental account to meet outstanding bills of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

It was voted to transfer $75.00 from incidental account to meet outstanding bills of *Chemical Abstracts*.

It was voted that the Finance Committee be given authority to transfer at their discretion from one account to another within a single appropriation.

The directors then considered the various estimates for expenditures and receipts for 1911 and approved an estimate to be forwarded to all members of the Council for their consideration previous to the Minneapolis meeting.

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It was voted that the treasurer be authorized to destroy at his discretion any vouchers or correspondence over five years old.

It was voted that the treasurer be given authority to transfer the safety deposit box of the Society from the Mercantile Safety Deposit Company to the vaults of the bank of the Metropolis.

The meeting then adjourned. CHARLES L. PARSONS,
Secretary.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

PUGET SOUND SECTION.

The October meeting was held at the Commercial Club, Tuesday, October 25th, at 8.00 o'clock, with the following program:

"The Geology of Cement Making Material," by I. F. Laucks. "The Manufacture of Portland Cement," by Chas. H. Newhall. "Composition and Uses of Cement," by L. H. Provine.

The November meeting was held at the "Faculty Club House," University of Washington, Saturday, November 26th, at 8.00 P.M.

The papers of the evening were: "Student Life among the Chemists in Germany," by Dr. Horace G. Byers. "A Report on the Cause of Corrosion in the Pipes of the Steam Heating System of a Large Building," by M. J. Falkenburg. A. JACOBSON, *Secretary.*

CORNELL SECTION.

The first meeting of the University year was held in Morse Hall, at 8.00 P.M., Wednesday, November 2nd. The program consisted of two reports: "The Amer. Chem. Soc. Trip to California," by Dr. Wilder D. Bancroft. "Some Recent Advances in Chemistry in Germany," Dr. William R. Orndorff.

The December meeting was held on Wednesday, December 7th, at 8.00 P.M., in Lecture Room No. 1. The program consisted of the following papers: "A Modified Reagent for the Determination of Nitrates," by D. S. Pratt. "The Chemical Behavior of Ammonium Trinitride in Liquid Ammonia at 33°," by A. E. Houlehan. "Chemistry in China," by M. J. Brown. Singing was enjoyed at the close of each meeting.

J. C. ANDREWS, *Secretary.*

CINCINNATI SECTION.

On November 12th the Cincinnati Section held a joint meeting with the Sections of the Middle West, the Cincinnati, Columbus, Cleveland, Indiana, Louisville and Chicago Sections being represented. There were

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117 present at the dinner given in honor of President W. D. Bancroft at the Hotel Sinton.

The speakers were: Address, Joseph W. Ellms, President Cincinnati Section; Address of Welcome, Dr. John Uri Lloyd, the author chemist. Addresses by guests of honor: Prof. Ira Remsen, of Johns Hopkins University; Dr. Chas. W. Dabney, President University of Cincinnati; Prof. John L. Shearer, President Ohio Mechanics Institute; Prof. A. Obenhommer, Professor of Geography, University of Vienna; W. D. Richardson, Editor *Journal of Industrial and Engineering Chemistry;* A. M. Patterson, Editor *Chemical Abstracts*; Addresses by representatives of the visiting sections. Response for the Cincinnati Section, Dr. Alfred Springer. Address: "The Measurement of High Temperatures in the Electric Furnace," Prof. W. D. Bancroft, President of American Chemical Society.

Throughout the day the visitors were entertained by visits to all the points of much interest in our vicinity, including The Cincinnati Filtration Plant, University of Cincinnati, Rockwood Pottery, Lloyd Library, Lunkenheimer Co., Merril Chemical Co., Globe Soap Co. and others. The meeting was an entire success from all point of view.

The 164th regular meeting of the Section was held in the Chemical Lecture Room of the Ohio Mechanics Institute on Wednesday, December 14th, at 8.00 P.M.

The paper for the evening, entitled "The Action of Alkalies on the Hexose Sugars," was by Dr. F. W. Upson, followed by a general discussion of the subject. A report of the Joint Meeting Committee was given by Dr. L. W. Jones, *Chairman.*

The following officers were elected for the year 1911: *President*, Max H. Goettsch; *Vice-Presidents*, O. H. Wurster, Sigmund Waldbott; *Recording Secretary*, Alfred Smith; *Financial Secretary*, B. M. Pilhashy; *Executive Committee*, L. W. Jones, H. E. Newman, Carlos Long; *Councilor*, Alfred Springer.

ALFRED SMITH, *Secretary.*

ST. LOUIS SECTION.

The second meeting of the fall was held on November 14th at the Academy of Science Building.

The program of the evening was as follows: "The San Francisco Meeting," by R. Norris Shreve. "A Brief Description of the Fontactoscope," by E. H. Keiser. "Tungsten," by George W. Wallace.

The annual meeting of the Section and that of the affiliated St. Louis Chemical Society was held on December 12th, at the Academy of Science Building. Mr. H. E. Wiedemann addressed the Societies on the subject of "Commercial Fertilizers." The St. Louis Section elected the following

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officers: Dr. E. H. Keiser, *President;* Mr. W. F. Monfort, *Vice-President;* Dr. S. H. Baer, *Treasurer;* Mr. R. Norris Shreve, *Secretary;* and Dr. C. E. Caspari, *Councilor.*

R. NORRIS SHREVE, *Secretary.*

ILLINOIS SECTION.

The following papers were presented to the Section on November 15th: "Derivatives of Isocamphoric Acid," by W. A. Noyes and Luther Knight. "The Spontaneous Combustion of Coal," by S. W. Parr and F. W. Kressman.

GRINNELL JONES, *Secretary.*

PHILADELPHIA SECTION.

The regular monthly meeting of the Section was held at the John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, on November the 17th.

The following were elected as Councilors for the Section for the ensuing year: G. E. Barton, W. T. Taggart, D. W. Horn.

The program consisted of an address by Dr. Hugo Schweitzer, of New York City, on "Erlich's Chemotherapy—A New Science, the Treatment of Diseases with Coal Tar Products and Arsenic Coal Tar Preparations."

C. S. BRINTON, *Secretary.*

SYRACUSE SECTION.

The sixty-first meeting was held at the College of Medicine, Friday, November 18th, at 8.00 P.M., in the form of a Symposium on Municipal Water Supply.

"Water Supply and the Typhoid Epidemic," by Dr. W. W. Waite, city bacteriologist. "The Influence of Certain Dissolved Minerals on the Potability of Water," by W. M. Booth. "How Conclusive is the Evidence drawn from the Analysis of Drinking Water?" by Professor Ernest N. Pattee. A general discussion followed.

A second symposium was held Friday, December 9th, at 8.00 P.M., at the Medical College, the subject for discussion being "Ammonia." The following attractive program was presented: "Manufacture of Ammonia," by Mr. C. G. Tufts. "Impurities in Ammonia," by Mr. Geo. Terziev. "Uses for Ammonia," by Dr. Louis C. Jones. "Ammonia for Refrigeration," by Mr. E. Austin Barnes.

W. H. MCLAUCHLAN, *Secretary.*

LOUISIANA SECTION.

The Section held its forty-fourth meeting at the Directors' Room of the Board of Trade, New Orleans, Friday, November 18th, at 8.00 P.M. The address was on "Some Chemical Problems in Medicine," by Dr. I. I. Lemann.

GEO. B. TAYLOR, *Secretary.*

KANSAS CITY SECTION.

The November meeting of the Section was held in the Chemistry Build-

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ing, University of Kansas, at Lawrence, on Saturday evening, November 19th, at 4.30 P.M.

At the first session, Mr. E. R. Weidlein gave a lecture on the "Whaling Industry." Mr. Weidlein spent part of last summer in Labrador and showed lantern slides illustrating some of his observations.

After supper, Dr. George B. Frankforter, Head of the Chemistry Department, University of Minnesota, lectured on "Waste Wood Products."

The annual election and banquet of the Section was held at the Y. M. C. A. Building, Kansas City, Mo., on Saturday evening, December 10th, at 6.30 P.M.

During the evening Prof. E. H. S. Bailey gave a report of the proceedings of the Association of Food Chemists at New Orleans and Prof. F. W. Bushong addressed the Section on "Petroleum Refining."

E. A. WHITE, *Secretary.*

CLEVELAND SECTION.

The November meeting was held in the Physics Laboratory, Case School of Applied Science, Monday, November 14th, at 8.00 P.M. The paper of the evening was by Professor D. T. Wilson on "Solar Chemistry."

The Section held an informal dinner in honor of Dr. Harvey W. Wiley, Chief of the Bureau of Chemistry of the United States Department of Agriculture, at the University Club, 2738 Prospect Ave., on Friday evening, November 25th, at 5.30 P.M.

The December meeting was held at Wohl's Restaurant, Monday, December 12th, at 6.30 P.M. After a paper by Dr. A. W. Smith, on "Some Technical Chlorine Products." The following officers for the coming year were elected: *President*, John W. Brown; *Secretary-Treasurer*, W. R. Veazey, Case School of Applied Science; *Councilors*, L. C. Drefahl and I. Ladoff; *Board of Managers*, A. L. Stark and D. B. Cleveland.

W. R. VEAZEY, *Secretary.*

CHICAGO SECTION.

The November meeting was held in the rooms of the Western Society of Engineers, 1735 Monadnock Building, on Friday evening, November 25th, at 8.00 P.M. The following officers were elected for the coming year: *Chairman*, S. T. Mather; *Vice-Chairman*, Otto Eisenschiml; *Secretary*, D. K. French; *Treasurer*, H. McCormack; additional member of the *Executive Committee*, W. D. Richardson; *Councilors*, Wm. Brady, Julius Stieglitz, A. Lowenstein.

The program of the evening was a symposium on cement. "Portland Cement as a By-product," by J. H. Kempster. "Non-Staining Cement," by John Moore. "Chemistry of Portland Cement," by George P. Dieckmann. Mr. Richard L. Humphrey, of Philadelphia, opened the general discussion.

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The December meeting will be held in the Kimball Café, 143 Monroe St., on Friday evening, December 16th, at 8.00 P.M.

The program of the evening was in the form of a symposium on paint. "The Manufacture and Valuation of Red Lead," by Mr. Clifford D. Holley. "The Development of Modern Paint Formulae," by Mr. L. S. Hughes. "Some of the Problems Confronting Paint Manufacturers and Paint Consumers," by Mr. Frank S. Low. "Paint Testing from a Physical Standpoint," by Mr. Hans Mannhardt.

Mr. O. Eisenschiml led the discussion and was followed by Mr. Ray Evans, of the Picher Lead Company.

A. L. NEHLS, *Secretary.*

MILWAUKEE SECTION.

The Section held an informal meeting at the Hotel Blatz on November 29th. In the absence of a regular program each member gave a short talk about some of the troubles he has had and how he has overcome them. An effort was made to have a large representation at the Minneapolis meeting.

BEN L. SALOMON, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club on Thursday evening, December 1st, preceded by dinner at 7 P.M.

The speaker for the evening was Dr. H. J. Wheeler, Director of the R. I. Experiment Station at Kingston, who gave a lecture on "A Review of Some Recent Work at the Rhode Island Agricultural Experiment Station."

ALBERT W. CLAFLIN, *Secretary.*

LOUISVILLE SECTION.

The December meeting of the Section was held on the 5th at the Galt House. Dinner was served at 6.30 P.M., followed by the regular order of business. The paper of the evening was by Mr. J. S. Cooper on "Paints."

F. F. HASBROUCK, *Secretary.*

MINNESOTA SECTION.

The regular meeting of the Section was held Tuesday evening, December 6th, at 8.00 P.M., in the Chemical Laboratory of the University of Minnesota. The program consisted of election of officers. Reports of committees preparing for the winter meeting of the society.

FRANCIS C. FRARY, *Secretary.*

WASHINGTON SECTION.

The two hundred and second meeting was held at the Cosmos Club, Thursday, December 8th, at 8.00 P.M. The following program was presented: "The Presence of Barium in Soils and Plants," by G. H. Failyer. "A Field Study of the Relation of Barium to the Loco-Weed Disease," by C. D. Marsh. "The Relation of Barium to the Loco-Weed Disease," by C. L. Alsberg and O. F. Black.

J. A. LECLERC, *Secretary.*

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SECTION OF EASTERN NEW YORK.

The annual meeting was held at President Ellery's home in the South College, Union College Campus, on Friday evening, December 9th, at 8.00 P.M. The following were elected officers for 1911: *President*, John Hurley; *Vice-President*, F. C. Zapf; *Secretary-Treasurer*, G. R. Fonda, Schenectady; *Councilor*, A. T. Lincoln; *Executive Committee*, Edward Ellery, B. S. Bronson, A. D. Carrier.

After the business meeting Prof. and Mrs. Ellery received the members of the Section and ladies.

R. C. ROBINSON, *Retiring Secretary.*

INDIANA SECTION.

At the meeting of the Section held Friday evening, December 9th, Mr. H. E. Barnard resigned as Councilor from the Local Section and Prof. John White, Terre Haute, Ind., was elected as Councilor for the unexpired term ending January 10th.

The papers of the evening were "Alloys of Cobalt and Chromium," by Elwood Haynes, Kokomo, Ind., and "Some Observations on the Accuracy of the Modified LaWall-Bradshaw Sodium Benzoate Method," by W. D. MacAbee, Indianapolis.

A. D. THORBURN, *Secretary.*

NEW YORK SECTION.

The second regular meeting of the session of 1910–'11 was held on November 11th.

The following papers were presented: "The Electron Conception of Valence," by K. G. Falk and J. M. Nelson. "The Influence of Vapors on the Surface Tension of Mercury," by Morris Loeb and S. R. Morey. "Electrochemical Oxidation of Some Hydrazine Salts" and "The Electrochemical Corrosion of Some Metals in Sodium Trinitride," by J. W. Turrentine and Willis A. Gibbons. Following these papers, Mr. Henry G. Pearson, editor of the *India Rubber World*, gave an illustrated lecture on "The Rubber Country of the Amazon."

The third regular meeting of the Session of 1910–'11 was held at the Chemists' Club on December 9th, in conjunction with the American Institute of Chemical Engineers, who were holding a general meeting in New York at the time.

Before proceeding to the subject of the evening, the Section held its election of Local Councilors and elected the following members: Chas. Baskerville, Morris Loeb, T. J. Parker, E. G. Love, P. C. McIlhiney, Wm. H. Nichols and Geo. C. Stone.

Prof. Baskerville, Chairman of the Section, called on Dr. F. W. Frerichs and Prof. J. C. Olsen, President and Secretary of the American Institute of Chemical Engineers, to sit on the rostrum when Dr. Frerichs made a short address on the relation between the society he represented and the American Chemical Society.

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The chairman announced the subject for the evening, "A Symposium on Sewage Disposal," and introduced the following speakers: Geo. C. Whipple, "The Principles of Sewage Disposal." Rudolph Hering, "Sewage Disposal in Europe." Geo. A. Soper, "Sewage Disposal in New York and Vicinity." Nicholas S. Hill, Jr., "Sanitary Conditions in their Relation to the Water Supplies in the Vicinity of New York." Chas.-E. A. Winslow, "The Unsolved Problems of Sewage Disposal."

Discussion of the subject followed by G. W. Fuller, Geo. A. Soper, Geo. F. Webster and Rudolph Hering.

C. M. JOYCE, *Secretary.*

WISCONSIN SECTION.

The annual meeting of the Section was held at Madison on Wednesday, December 14th, at 8.00 P.M., in Room 113 of the Chemistry Building. Professor A. S. Loevenhart presented a paper on "The Pharmacological Action of Iod, Iodoso and Iodoxy Benzoic Acids."

E. V. MCCOLLUM, *Secretary.*

SECTION OF WESTERN NEW YORK.

The Section met on Wednesday, December 14th, at the University of Buffalo, Buffalo, at 8.00 P.M.

There was no set subject, but every member was requested to come prepared to deliver a short talk on some observation, experiment, device, or experience of his own for the benefit of fellow members.

An informal supper preceded the meeting.

W. WALLACE, *Secretary.*

PITTSBURGH SECTION.

The regular meeting of the Section was held in Thaw Hall, University of Pittsburgh, Grant Boulevard, on Thursday evening, December 15th, at 8.00 P.M.

The paper of the evening was on the "Operation and Enforcement of the Food and Drugs Act of June 30th, 1906," by M. C. Albrech, Chief of U. S. Food and Drug Laboratory, Pittsburgh.

JOHN A. SCHAEFFER, *Secretary.*

NORTHEASTERN SECTION.

The December meeting of the Section, being the one hundredth regular meeting, was celebrated by a dinner, held on Friday, December 16th, at 6.30 P.M., at the Exchange Club, Boston. The evening was devoted to a consideration of the important subject, "Conservation of Our National Resources."

Professor J. A. Holmes, Chief of the Bureau of Mines, Washington, D. C., gave an address upon "Work of the Bureau of Mines in Relation to the Conservation of Our Resources," and Hon. Curtis Guild, Jr., Ex-Governor of Massachusetts, spoke upon "Conservation."

Officers for the coming year were elected as follows: *President,* Walter

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L. Jennings; *Vice-President*, Lyman C. Newell; *Secretary*, Warren K. Lewis; *Treasurer*, Hermann C. Lythgoe; *Executive Committee*, William C. Bray, G. Shannon Forbes, William W. Duncan, Kenneth L. Mark, J. W. Phelan; *Councilors*, Francis E. Gallagher, Henry P. Talbot, Leonard P. Kinnicutt, Salmon W. Wilder, Gilbert N. Lewis.

KENNETH L. MARK, *Secretary*.

IOWA SECTION.

The November meeting was held in the Chemical Lecture Room of the State University of Iowa, at Iowa City, on Saturday, November 12th, at 9 A.M.

The following program was presented: "The Effect of Continued Grinding on the Water of Crystallization," by Professor Nicholas Knight, Cornell College. "The Effect of the Mechanical Arrangement of the Rotary Kiln and its Manipulation on the Chemical Composition of the Mix and Resulting Clinker," by Mr. Roy P. Tucker, Iowa Portland Cement Co., Des Moines, Ia. "Chemical Courses and Chemical Industries," by Dr. L. W. Andrews, Andrews Chemical Works, Davenport, Ia. Miscellaneous Reports.

J. N. PEARCE, *Secretary*.

DECEASED MEMBERS.

Rudolph Fittig, November 22, 1910, University of Strassburg, Strassburg, Germany.

Clarence W. Beaver, San Francisco, Cal.

E. P. Coleman, Buffalo, N. Y.

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A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.

(FIRST PAPER.)

THE ANALYSIS OF NEODYMIUM CHLORIDE.

BY GREGORY PAUL BAXTER AND HAROLD CANNING CHAPIN.

Received October 29, 1910.

CONTENTS.—Introduction. The Separation of Neodymia from Other Rare Earths. The Absorption Spectrum of Aqueous Solutions of Neodymium Salts. The Preparation of Neodymium Chloride. The Preparation of Pure Silver. The Drying of the Neodymium Chloride. The Method of Analysis. The Determination of the Moisture Retained by the Neodymium Chloride. The Specific Gravity of Neodymium Chloride. Results and Discussion. Summary.

Introduction.

Investigations bearing upon the rare earths have always been particularly attractive on account of some unusual chemical and physical properties of these substances, their peculiar relations to the Periodic System, and in particular the important position which some of them have taken with relation to artificial illumination. To be sure any research involving the preparation of even one of the earths in a state of approximate purity is sure to be protracted, if not tedious. The very proof of the purity of a preparation is by no means easy to secure. The chief guides which have served in the determination of the purity of material have been the spectra, both absorption and emission, and the atomic weights. For a quantitative determination of purity the atomic weight is perhaps more frequently used than any other test. Hence for this reason, as well as from theoretical considerations, an exact knowledge of the atomic weights of the rare earths is very desirable.

The atomic weights of certain members of the group have received a singularly large amount of attention. Those of cerium and lanthanum,

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for instance, have been investigated more times than that of iron. Yet owing to the unusual difficulties in the preparation of pure material, as well as to troublesome analytical problems, the determinations of the atomic weights of the rare earths are probably of a lower order of accuracy than those of the common elements.

Among the standard methods which have heretofore been employed in the determination of atomic weights of the rare earths, the following are the most important.

The Analysis of the Oxalate (Stolba[1]).—The dried oxalate is analyzed for the oxide by ignition, and for oxalic acid by titration with permanganate. The complete analysis of the salt is necessary on account of the invariable presence of an uncertain amount of crystal water even in the dried salt. Gibbs[2] has pointed out, on account of irregularity in the water content, the necessity of grinding thoroughly the whole specimen of oxalate which is to be used for analysis, in order to insure homogeneity of material. Furthermore, it has been shown by Baxter and Griffin[3] and Baxter and Daudt[4] that the oxalate must be precipitated in acid solution, since in neutral or alkaline solution the oxalates of the alkalis and ammonium are carried down by the rare earth oxalate in considerable quantities. Brauner[5] has found that in some cases at any rate the oxalate hydrolyzes in contact with water, although the magnitude of the latter error is doubtful. In spite of these difficulties the oxalate method is as easy to carry out as any and probably the most satisfactory for approximate purposes.

The Analysis of the Sulfate.—The sulfates have been used for atomic weight purposes in several ways. Bahr and Bunsen[6] first employed the method of dissolving weighed amounts of oxide in sulfuric acid and weighing the sulfate after expelling the excess of acid. By the ignition of the oxalate it is doubtless possible to prepare the oxides in a very pure state if great care is taken to protect them from access to moisture or carbon dioxide, at any rate with elements which form trivalent compounds only. To prepare the sulfate in a neutral dry condition is a much more difficult proposition, owing to the retention of water and sulfuric acid if the temperature of heating is low, and to decomposition with loss of sulfuric acid at higher temperatures. The investigations of Bailey,[7] Kruss,[8]

[1] *Sitzungsber. böhm. Ges.*, Dec., 1878.

[2] *Proc. Am. Acad.*, 28, 261 (1893).

[3] THIS JOURNAL, 28, 1684 (1906).

[4] *Ibid.*, 30, 563 (1908).

[5] *J. Chem. Soc.*, 81, 1266 (1902).

[6] *Lieb. Ann.*, 137, 5 (1866).

[7] *J. Chem. Soc.*, 51, 683 (1887).

[8] *Z. anorg. Chem.*, 3, 46 (1893).

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Jones,[1] Brauner,[2] Wild,[3] Brill,[4] and Holmberg[5] leave this matter still in a somewhat unsettled state.

The difficulty in obtaining the anhydrous sulfate in a neutral condition applies also to the method of ignition of sulfate to oxide. Furthermore, it is probable that the oxide prepared by ignition from the sulfate retains traces of sulfuric acid.[6]

A third method depending upon the use of the sulfates involves the determination of the water in the octahydrated sulfate. Here the difficulty in obtaining crystals free from included cells of mother liquor is superimposed upon that of insuring complete dehydration.

The Analysis of the Chloride.—The analysis of the chloride has been little used on account of the tendency for the formation of insoluble basic compounds during drying. As Matignon[7] has pointed out, if the dehydration of the chloride is conducted slowly and thoroughly enough in an atmosphere of dry hydrochloric acid gas, this difficulty disappears and a perfectly soluble product can be obtained, even after fusion. Hence, on account of the accuracy with which halogen salts may be analyzed by precipitation with silver, this method is one of the best for atomic weight purposes. In testing the applicability of this method, we chose neodymium chloride for investigation, since neodymium compounds are comparatively easy to secure in an approximately pure state in large quantities. Furthermore, unlike its close relation, praseodymium, neodymium does not readily change from the trivalent state.

Historical.—The atomic weight of neodymium has already been determined many times, with discrepant results. This element and praseodymium, the other component of the old didymium, were first separated through the fractional crystallization of the double ammonium nitrates by Auer von Welsbach[8] in 1885. He determined their atomic weights by Bunsen's method of converting oxide to sulfate, but apparently interchanged his results in publication, as first suggested by Brauner, as he gave the value 140.8 for neodymium and 143.6 for praseodymium.

In 1898 Brauner,[9] by converting oxide to sulfate, obtained the result 143.6 for neodymium. In this he included a correction for an impurity of 2.9 per cent. of the corresponding praseodymium compound, estimated by comparison of the intensity of absorption spectra.

[1] *Am. Chem. J.*, 28, 31 (1902).
[2] *J. Chem. Soc.*, 81, 1248 (1902).
[3] *Ibid.*, 38, 195 (1904).
[4] *Ibid.*, 47, 464 (1905).
[5] *Z. anorg. Chem.*, 53, 124 (1907).
[6] Brauner, *Loc. cit.*, 1263.
[7] *Compt. rend.*, 133, 289 (1901); 140, 1182 (1905).
[8] *Sitzungsber. Akad. Wiss. Wien*, 92, 317 (1885).
[9] *Proc. Chem. Soc.*, 14, 70 (1898); *Chem. News*, 77, 161 (1898).

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In the same year Boudouard[1] obtained a neodymium preparation by precipitation with potassium sulfate from some impure yttrium material. Apparently to identify the base rather than to establish its atomic weight, he analyzed the sulfate by converting it to oxide, with the result 143.0. Undoubtedly his material contained praseodymium, as no steps were taken to remove this inevitable impurity.

In 1898 Jones[2] also investigated both neodymium and praseodymium with material purified by crystallization as the double ammonium nitrate. Cerium and lanthanum were eliminated by precipitation as basic nitrates, and a correction for residual praseodymium was obtained by comparing the intensities of its absorption bands in the neodymium preparations with those of the same bands in dilute praseodymium solutions of known strength. The atomic weight was found by converting the oxide to sulfate. The average of twelve results, ranging in value from 143.46 to 143.62, was 143.55. Corrected for praseodymium content this value becomes 143.60.

In 1901, after further purification of his original material, Brauner[3] published another determination, which yielded the value 143.89. As this is the result of but one analysis and includes a correction of questionable accuracy for praseodymium impurity, it can hardly be given much weight.

Auer von Welsbach,[4] in 1903, published the results of further study of both neodymium and praseodymium. His source of material was a large quantity of double ammonium nitrates obtained as by-products in the technical extraction of lanthanum. A long series of fractional crystallizations as double ammonium nitrate served to free the neodymium from all but a trace of praseodymium. With this material, undoubtedly of very high purity, three analyses were made by the Bunsen method of converting oxide to sulfate, from which the atomic weight values 144.55, 144.52, and 144.57, respectively, were obtained. Unfortunately, no details of procedure are given.

A point of especial interest in connection with Jones's and Brauner's results is Auer's observation that the praseodymium absorption spectrum is weakened considerably by lanthanum and cerium ammonium nitrates and other salts, as well as by concentrated nitric acid, the effect of which was mentioned in Auer's earlier paper. Clearly any quantitative comparison of the intensity of the praseodymium spectrum from solutions of praseodymium salts alone, with that from solutions consisting mainly of other rare earth salts, is unreliable.

[1] *Compt. rend.*, 126, 900 (1898).
[2] *Amer. Chem. Jour.*, 20, 345 (1898).
[3] *Proc. Chem. Soc.*, 17, 66 (1901).
[4] *Sitzungsber. Akad. Wiss. Wien*, 112, 1037 (1903).

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Feit and Przibylla[1] dissolved weighed amounts of various rare earth oxides in sulfuric acid and titrated the excess of acid, using methyl orange as the indicator. The end point was interfered with by the pink color of the neodymium salt, but this difficulty was obviated by comparing the solutions with standards containing the same amounts of indicator and neutral neodymium salt. Their neodymium material was prepared by fractional crystallization of the double magnesium nitrate. This preparation showed no trace of the strongest praseodymium and samarium absorption bands, although the "hellblau" color of the oxide was considered the best proof of its purity. The result for the atomic weight of neodymium was 144.60.

Holmberg,[2] after a study of the rare earth salts of twelve organic acids, selected the metanitrobenzene sulfonate as particularly suitable for the purification of neodymium, and by one hundred and sixty-two series of crystallizations obtained thirteen fractions ranging in atomic weight from 144.0 to 145.3. The purest fractions were selected and the oxide obtained by ignition of the oxalate was weighed and converted into sulfate. The value 144.10 was obtained as the mean of six results varying from 144.03 to 144.15.

The International Committee on Atomic Weights have chosen as the most probable value 144.3, which represents an average of the more recent determinations.

The Separation of Neodymia from Other Rare Earths.

It is a well-known fact that when a salt of a mixture of rare earths is subjected to fractional crystallization, the less soluble salts tend to concentrate at the less soluble end of each series of fractions, and the more soluble salts at the opposit end of the series. In most cases it is less difficult to free an earth very thoroughly from more soluble impurities than it is to eliminate impurities which tend to concentrate in the crystals. An obvious although not generally recognized way out of the difficulty is to crystallize the substance in such different forms that impurities which tend to concentrate in the crystals in one case, concentrate in the mother liquors in another, continuing the crystallization in any one form until impurities which accumulate in the mother liquors have been eliminated as completely as possible.

In the present instance the material was crystallized first as double ammonium nitrate from dilute nitric acid, then as nitrate from concentrated nitric acid. According to Auer von Welsbach,[3] in crystallization as double ammonium nitrates the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium and yttrium

[1] *Z. anorg. Chem.*, 43, 202 (1905).

[2] *Ibid.*, 53, 83 (1907).

[3] *Sitzungsber. Akad. Wiss. Wien*, 112, 1043 (1903).

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earths, while, according to Demarçay,[1] in the crystallization of the nitrates from nitric acid the solubility first decreases with increasing atomic weight through gadolinium, 157.2, and then increases. In the crystallization as double ammonium nitrates samarium and the more soluble earths were eliminated, while in the crystallization of the nitrates from nitric acid the solubility of the first four of the above nitrates is reversed and the lanthanum, cerium and praseodymium were removed in the mother liquors.

Three and one-half kilograms of neodymium ammonium nitrate, very kindly furnished by Dr. H. S. Miner, of the Welsbach Light Company, served as a starting point in the preparation of pure material. The history of this material is somewhat uncertain, but, as nearly as can be determined, is as follows: Swedish cerite was decomposed with acid and the rare earths were precipitated as oxalates, from which the oxides were obtained by ignition. These oxides were then treated with nitric acid and the insoluble basic ceric salt was produced by heating. The lanthanum, praseodymium, neodymium, samarium, yttrium, etc., were obtained in solution. After the addition of ammonium nitrate the material had received, probably, about 150 to 250 crystallizations. Our treatment showed it to contain considerable lanthanum, cerium, and praseodymium, and a small amount of samarium. Probably traces of other rare earths were present, but no evidence of their existence was found even in the extreme fractions of the purified material.

In the further purification to which we subjected the double neodymium ammonium nitrate the usual method of fractional crystallization was followed: The whole material (1) was crystallized and the crystals (2) were separated from the mother liquor (3). The crystals were dissolved and again crystallized, the crystals becoming (4) and the mother liquor (5). The mother liquor (3) was evaporated to crystallization, and the crystals were combined with (5), while the mother liquor formed (6), and so on indefinitly. After the first few series of crystallizations the number of fractions in each series was maintained nearly constant between twenty and twenty-five, and the different fractions were not allowed to vary much in size. As a rule the solutions were allowed to become supersaturated by cooling without crystallization, then they were seeded with tiny crystals of the purest neodymium salt available, and allowed to stand undisturbed over night in order that by the formation of large crystals the removal of mother liquor might be facilitated. On account of the extra labor and time involved, centrifugal drainage of the crystals is of little advantage where the composition of crystals and mother liquor differs as slightly as in the present case, and therefore was not employed. When the end fractions become small they were either

[1] *Compt. rend.*, 122, 728 (1896); 130, 1021 (1900).

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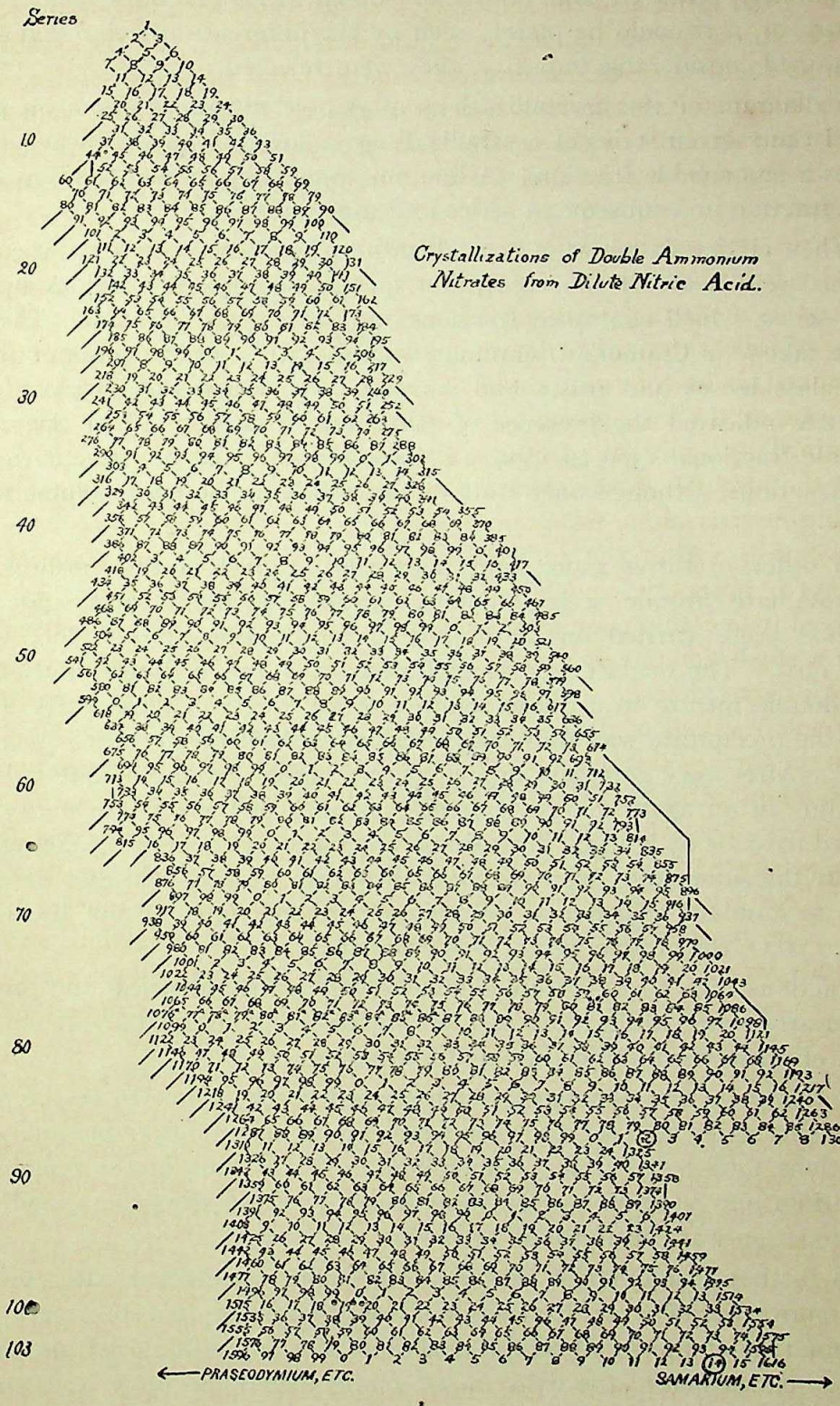


Fig. 1.

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temporarily removed and added to similar fractions subsequently obtained, or, if it could be plainly seen by the difference in color that they contained considerable impurity, they were rejected.

A diagram of the crystallizations as double nitrate is given on page 7. In any given series of crystallizations a lower number always indicates a less soluble fraction. A line not connecting an end fraction with any fraction in a subsequent series indicates rejection.

When eighty-six series of crystallizations had been completed, spectrograms were made of the absorption spectra of selected fractions in the last series, which contained fractions 1287 to 1309. These photographs were taken on Cramer's trichromatic plates with a spectrograph employing glass lenses and prism and covered the range $\lambda 650$–$\lambda 380$. The spectra indicated the presence of samarium in only a few of the more soluble fractions, 1306 to 1309. Praseodymium could be detected in all the fractions, although only traces were visible in the more soluble fractions.

In order to throw more light upon the progress of the purification, approximate atomic weight determinations by the "permanganate" method were carried out with portions of fractions 1290, 1299, 1303 and 1305. The oxalate was precipitated by adding a dilute solution of the double nitrate to a dilute solution of an excess of pure oxalic acid, and the precipitate was thoroughly washed, collected, and dried at 120–130°. After very complete mixing of the highly crystallin material by grinding in an agate mortar, weighed portions of the oxalate were converted to oxide by ignition in platinum crucibles. Other portions, weighed out at the same time, were dissolved in dilute sulfuric acid and titrated with a standard solution of potassium permanganate. From the ratio $M_2O_3 : 3C_2O_4$ the atomic weight was calculated.

Fractions 1299 to 1305 were evidently very nearly identical and probably nearly pure, while fraction 1290 apparently contained about ten per cent. of praseodymium, cerium and lanthanum.

At this point fraction 1302, which seemed on the whole to be the purest in this series, was set aside for more careful examination and analysis. Fractions 1303 to 1309 also, which contained the bulk of the remaining samarium and yttrium earths, were separated from the others, and the fractionation was continued as before.

No further accumulation of samarium could be detected, after seventeen more series of crystallizations had been completed, in a spectrographic examination of the more soluble fractions of the one hundred and third series. Nevertheless the two most soluble fractions, 1615 and 1616, were rejected, and the next, 1614, was removed for subsequent analysis.

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Fraction.		Proportion of Nd_2O_3.	Proportion of C_2O_4.	Atomic weight.
1290		0.5334	0.4193	.....
		0.5334	0.4194	.....
		.....	0.4195	.....
	Average,	0.5453	0.4194	143.9
1299		0.5454	0.4274	.....
		0.5452	0.4281	.....
		.....	0.4278	.....
		.....	0.4279	.....
	Average,	0.5453	0.4278	144.3
1303		0.5412	0.4258	.....
		0.5412	0.4258	.....
	Average,	0.5412	0.4258	143.8
		0.5391	0.4217	.....
		0.5390	0.4228	.....
		.....	0.4218	.....
		.....	0.4221	.....
	Average,	0.5390	0.4221	144.6
		0.5379	0.4212	.....
		.....	0.4212	.....
	Average,	0.5379	0.4212	144.6
			Average of second and third values,	144.6
1305		0.5447	0.4269	.....
		0.5448	0.4272	.....
		.....	0.4272	.....
		.....	0.4269	.....
	Average,	0.5448	0.4271	144.4
		0.5414	0.4236	.....
		.....	0.4242	.....
	Average,	0.5214	0.4239	144.6
			Average,	144.5

The sharpness with which the samarium is removed from the neodymium by the crystallization of the double ammonium nitrate is striking in comparison with the difficulty in eliminating the last traces of praseodymium in the same way: "After the removal of only eight fractions, 1302 to 1309, the last of which was comparatively rich in samarium, seventeen series of crystallizations failed to reveal any residual samarium. On the other hand, when the fractions 1303 to 1309 were subjected to further fractional crystallization by themselves, the least soluble frac-

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tion of the fourteenth series was found to contain about one-half per cent. of praseodymium, estimated spectrographically as described later. By the same method fraction 1302, which contained more praseodymium than any one of the seven crystallized, was found to contain only 0.2 per cent. of this impurity. Demarçay[1] and Feit and Przibylla[2] have emphasized the fact that neodymium and samarium may be separated with equal facility by crystallization as double magnesium nitrates.

At this point it seemed reasonably certain that practically all the more soluble rare-earth impurities had been eliminated, while evidence of praseodymium could still be seen in the absorption spectra of all the fractions. For the removal of the praseodymium and at the same time cerium and lanthanum, if present, crystallization of the nitrates from concentrated nitric acid was next undertaken, since in this process these elements accumulate in the mother liquors.[3]

The ammonium nitrate was removed from the different fractions by evaporation and ignition, concentrated nitric acid was added, and the crystallization was carried through sixty-seven series. The same numbering was continued, except that the order of the one hundred and third series was reversed to give the less soluble fractions the lower numbers as before, 1613 becoming 1613*a* and 1596 becoming 1630. During these sixty-seven series no fractions were rejected at the less soluble end, although the extreme mother liquor was frequently rejected. Thus any nitrate less soluble than neodymium nitrate would concentrate in the extreme crystal fraction of the last series. A diagram of this treatment follows.

The fractions of the last series, 2923 to 2945, were then converted to oxide by precipitation as oxalate from acid solution and ignition of the oxalate. The different fractions of oxide were all of the same lilac-blue color. We could detect no difference in the color of the oxides of fractions found to be essentially free from praseodymium and those containing several tenths of a per cent. of this impurity.

The final fractions were next subjected to careful comparative spectrographic examination, great pains being taken to have the conditions of experimentation the same for all the fractions. One gram of every third fraction was dissolved in nitric acid, and, after the excess of acid had been evaporated, the solutions were diluted to the same volume, about 5 cc. Photographs of the absorption spectra were made, the solutions being contained in test tubes of the same diameter, and various lengths of exposure being employed. The samarium band λ 401 was faintly visible in fraction 2923 only. This is not surprising, however,

[1] *Compt. rend.*, 130, 1021 (1900).
[2] *Loc. cit.*, p. 207.
[3] Demarçay, *Loc. cit.*

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since, as has been stated before, no fractions had been removed from the less soluble end of the series in the course of all the sixty-seven series of crystallizations from concentrated nitric acid. Praseodymium could

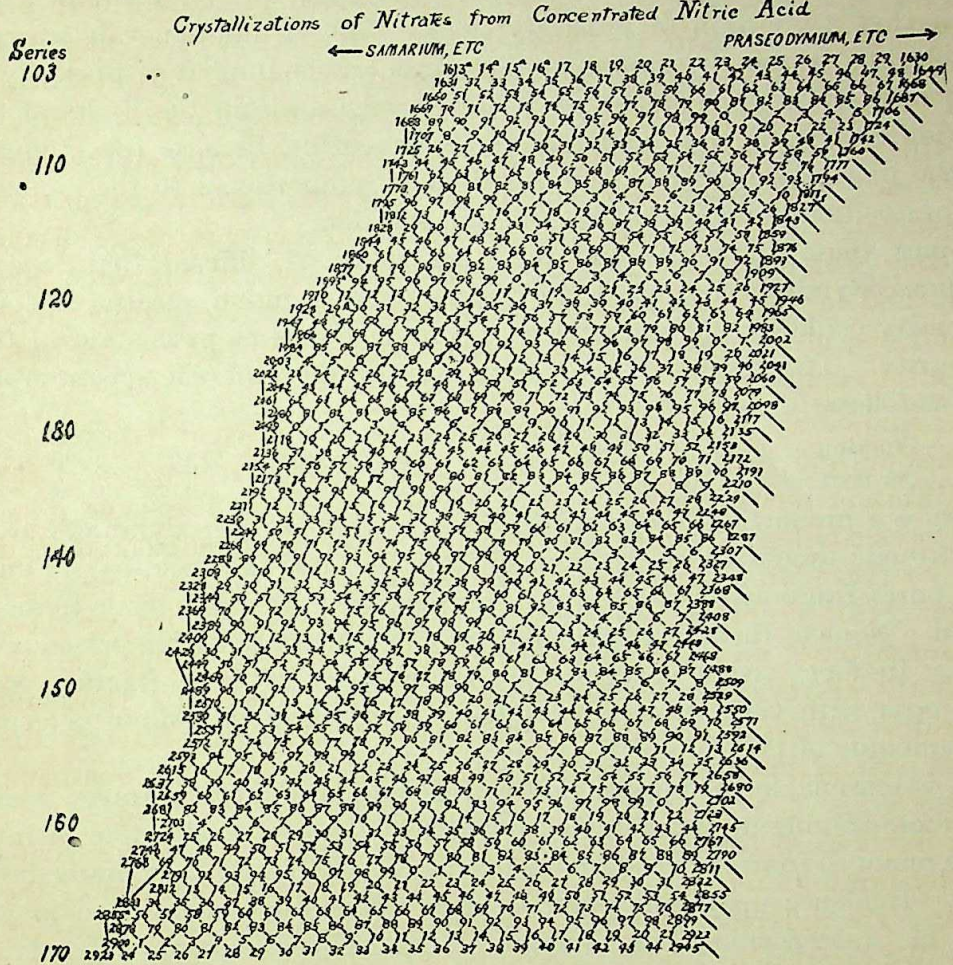


Fig. 2.

not be detected in fractions 2923 to 2932, but its strongest absorption band, λ 444, appeared with regularly increasing intensity in fractions 2935 to 2944.

In order to find out how much praseodymium can be detected in this way, and at the same time to estimate the proportion of praseodymium in the latter fractions, spectrograms were made, on one plate, and with the same exposure, of the spectra of most of the solutions previously examined, and also of others similarly prepared from fractions 1302 and 1614, which had been removed at earlier stages of the fractionation. To a solution of fraction 2926, in which no praseodymium could be detected in the first photograph, 0.1 per cent. of praseodymium oxide was added in solution, and the original concentration was restored by evaporation. The absorption spectrum of this specimen was photographed

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on the same plate as above, and again after the praseodymium content had been increased to 0.2, 0.5 and 1.0 per cent., respectively. In the negative the first addition of 0.1 per cent. made a distinct impression. From this it was concluded that fractions 2923 to 2932 contained less than that proportion of praseodymium. This assumption can scarcely be objected to on the ground that a considerable amount of praseodymium in fraction 2926 might have been brought within the limits of detection by means of a relatively small increment, because the intensity of the praseodymium band appeared to be proportional to the amounts of praseodymium added to the original solution.

Since these standards and the other solutions differed little except in praseodymium content, those giving praseodymium spectra of equal intensity could be safely assumed to contain the same percentage of this impurity. The results of the comparison of the different spectrograms are as follows:

Fraction.....	2935	2938	2941	2944	1302	1614
Per cent. of Pr	0.05	0.1	0.2	0.5	0.2	0.15

Since a proportion of one-tenth of a per cent. of praseodymium lowers the atomic weight of neodymium by only four one-thousandths of a unit, the purer fractions were obviously as pure as it is worth while to make them. None of them in all probability were entirely free from praseodymium. In fact, visual spectroscopic examination of both fraction 2929 and 2931 with very strong absorption showed them to contain perceptible amounts of this impurity.

It is reasonable to suppose that cerium and lanthanum nitrates, which are more soluble in concentrated nitric acid than praseodymium nitrate, were removed from the neodymium even more completely than praseodymium. Evidence upon this point is more difficult to secure than in the case of praseodymium, on account of the lack of absorption bands of cerium and lanthanum in the visible spectrum. The following test for cerium was carried out with fraction 2944, which contained 0.5 per cent. of praseodymium. The hydroxide was precipitated by the addition of an excess of sodium hydroxide, and, after washing by decantation, it was treated with saturated chlorine water for some time. A small quantity of undissolved hydroxide was filtered off and dissolved in nitric acid. To the nearly neutral solution a sufficient amount of a solution of calcium hypochlorite was added to produce a slight permanent precipitate. This precipitate was pink with no tinge of yellow. The same solution, after the addition of a trace of cerium and testing with hypochlorite as before, yielded a precipitate distinctly colored with the characteristic yellow of ceric hydroxide. Fraction 2944 was evidently nearly, if not entirely, free from cerium and the less soluble fractions of the series must have been purer still.

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The Absorption Spectrum of Aqueous Solutions of Neodymium Salts.

The absorption spectra of two of the purest fractions, 2929 and 2931, were examined visually with a Hillger wave-length spectroscope. While no very great accuracy is claimed for the measurements, it is probable that the values are correct within one-millionth of a millimeter, for the spectroscope is capable of nearly ten times this accuracy for wave lengths in the neighborhood of λ 500.

In the first two columns of the following table are given the values for the maxima of absorption observed during the gradual dilution of very concentrated, slightly acid solution of the nitrates, each value having been obtained in the most dilute solutions in which the band could be observed. The spectra of the two fractions were identical.

The band λ 580 can be seen only at certain medium concentrations

Baxter and Chapin fractions 2929 and 2931 (1909)	Forsling and Holmberg (1907).	Rech and Muthmann (1906).	Auer von Welsbach (1903).
...	.....	.....	745 to 725
689	689.5	.....	687
679	677.5	679.6	678
673	672.0	670.8	673
636	636.0	636.6	635
628	627.8	628.6	629
625	625.4	624.8	626
622	621.7	622.2	622
587	.....	586.5	...
583	.....	583.2	583
580	.....	580.8	...
578	578.8 to 578.0	578.5	579
575	575.4	575.4	579
574	573.5	573.6	575
571	571.6	571.7	572.5
547	.....	.....	567.5
531	532.3	532.0	532
525	.....	525.4	525
521	521.6	522.2	522.7
520	520.4	520.5	521
...	.....	514.5	...
512	512.4	512.2	511.7
509	508.7	508.9	508.3
487	489.0 to 486.0	488.0	...
480	479.9	479.8	...
475	474.8 to 474.2	475.4	475.4
469	468.7	469.0	469.6
461	461.0 ..	461.1	461
444 Pr	.....	444.2	...
433	433.0	434.2; 432.9	432
429	.....	429.5; 428.1	...
427.5	427.1	427.2	426.5
418	418.3	418.2	417.8

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while the band λ 547 is visible only with very concentrated solutions. The praseodymium band λ 444 also was faintly visible only in the most concentrated solutions. The two bands λ 580 and λ 547 disappear if the nitrate is changed to chloride; otherwise the nitrate and chloride give maxima in essentially the same positions, although the relative intensities of the bands are somewhat different in the two cases.

The third, fourth and fifth columns of the foregoing table represent the corresponding results obtained by Forsling from Holmberg's neodymium preparation,[1] by Rech from Muthmann's preparation,[2] and by Auer von Welsbach from his own material.[3] The last were taken from the drawings which were Auer's only published record, and since they are subject to two personal errors are less exact than the others. Being obtained, however, from very carefully prepared material, they should represent at any rate the number and the general location of the bands in the neodymium spectrum.

While some of these bands are sharp, and appear in the same positions in solutions of various concentrations, others fade away gradually on the edges, and sometimes have their maxima shifted by changes in the concentration. Consequently the disagreement as to the exact positions of bands is due in many cases merely to differences in the conditions of observation. Furthermore, Forsling and Rech used chloride solutions, whereas Auer von Welsbach and the writers used nitrate solutions. On the whole, the agreement between the different sets of values is very satisfactory. The bands between λ 587 and λ 571 are too close together to be distinguished from one another under any but the most favorable conditions. The double band λ 575 and λ 574 in particular separates only under rather limited conditions. The band at λ 579 in one of Auer's drawings may be intended to represent two lines at λ 580 and λ 577, and is thus interpreted by Kayser. Auer's band λ 567.5 appears very faintly in but one of his four drawings. There is a complete absence of shadow at this point in another drawing which represents a more concentrated solution, and which one would expect consequently to show the band. It is possible therefore that its appearance in the first print was merely accidental. The band λ 525 in concentrated solutions merges with λ 522 and in dilute it becomes invisible, so that it is not surprising that it was not observed by Forsling and Holmberg. The band λ 514.5, given by Rech alone, is coincident with no prominent band of any other rare earth, nor could it be detected in any of our preparations. The band λ 488, which both Forsling and Rech observed, as has already been stated, can be seen only with very strong absorption. This is doubtless the reason that it was not observed by Auer.

[1] *Z. anorg. Chem.*, 53, 83 (1907).
[2] *Z. Wiss. Photographie, Photophysik u. Photochemie*, 3, 411 (1906).
[3] *Sitzungsber. Akad. Wiss. Wien*, 112, 1037 (1903).

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The presence or absence of the predominant impurities, praseodymium, cerium, lanthanum and samarium, in our best material has already been discussed. It is of some interest to consider other earths having prominent absorption bands in the visible spectrum.[1] Since none of these could have been present in quantity, their absorption bands obviously could be found only in concentrated solutions. The marked broadening and running together of the neodymium bands in concentrated solutions makes the detection of bands due to impurities difficult, except when these occur in regions in the spectrum comparatively free from neodymium bands. Of the three strong erbium bands λ 650, λ 540, and λ 522, the last two are completely masked by the neodymium in concentrated solution. The band λ 650, however, occurs in a region favorable for observation, and could not be detected even in the most concentrated solution. In the case of holmium the three strongest bands, λ 639, λ 535, and λ 485, all fall within the limits of neodymium bands at high concentrations. There was no evidence of the strongest, λ 535, in solutions of average concentrations. The strongest dysprosium band λ 451, which falls just within the broad neodymium band λ 484–λ 453, as it appeared in our most concentrated solutions, could not be detected. The terbium band λ 488 practically coincides with the neodymium band 487, which could be seen in our preparations only at the highest concentrations. Since the band could be seen of the same intensity in all our preparations, it is improbable that it represents an impurity of terbium. The sharp thulium band λ 700 does not fall within the limits of any neodymium band, and we could find no evidence of its presence. Since the absorption of europium solutions in the visible spectrum is faint, and since all the stronger bands are masked completely by the bands of a concentrated neodymium solution, we have no spectroscopic evidence concerning the absence of this element. It may be added that, even in the extreme fractions of our crystal series, we could not detect the presence of any of these rarer elements. Further study of the absorption spectrum of neodymium is planned with the aid of a large quartz spectrograph, which has recently become available for us.

The Preparation of Neodymium Chloride.

The neodymium oxide fractions prepared as above were converted to chloride as follows: Fractions 1302 and 1614 were dissolved in the purest nitric acid in platinum vessels, the solutions were filtered, and the oxalate was precipitated from acid solution by means of the purest oxalic acid. After the oxalate had been washed by decantation and drained by suction upon a porcelain Gooch crucible employing a small disk of filter paper in place of an asbestos mat, the salt was dried and ignited in a

[1] The following data are obtained from drawings by Urbain, *J. chim. phys.*, 4, 31, 105, 232, 321 (1906).

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platinum dish over a blast lamp. The oxide was dissolved in a quartz dish in hydrochloric acid which had been distilled with the use of a quartz condenser, and the chloride was three times crystallized with centrifugal drainage in platinum Gooch crucibles[1] in each case. The crystal yield was brought to a maximum by treating the solution at 0° with hydrochloric acid gas obtained by warming concentrated solutions of the acid and led to the solutions through a quartz tube. Drying over sulfuric acid in a vacuum desiccator and powdering in an agate mortar completed the preparation for the final dehydration and analysis.

On account of the small quantity of material in each fraction of the final series, adjacent fractions were combined. The combinations actually analyzed were 2923–2924, 2926–2927–2928, 2932–2933, and 2936–2937. A suspicion of contamination by platinum during the ignition of the oxides in platinum led to a slight change in the purification of these fractions. The original oxide was dissolved in hydrochloric acid in a quartz dish, and hydrogen sulfide, generated by the action of sulfuric acid on ferrous sulfide and thoroughly scrubbed with water, was passed into the hot, slightly acid solution. A slight black precipitate of platinum sulfide was formed in every case. The oxalate was precipitated from the filtered and boiled solution, and was collected and dried as before. In the ignition of this oxalate an electrically heated quartz muffle, kindly loaned to us by Dr. H. H. Willard, was used. Since the temperature of the muffle was very uniform, a lower temperature could be employed for the decomposition of the oxalate. The product of decomposition, which contained a large proportion of carbonate when obtained in this way, was dissolved in hydrochloric acid in a quartz dish and was crystallized as before. The first mother liquor, which in the case of fractions 1302 and 1614 had been slightly tinged with yellow, was in the case of all the other fractions free from such evidence of dissolved platinum.

The Preparation of Pure Silver.

Pure silver was prepared by methods which have already been found to be very effective. Since these methods have been described in detail several times in papers from this laboratory,[2] only a brief outline of the processes is given here. Crude silver was dissolved in nitric acid, precipitated as chloride, reduced with alkaline invert sugar, and fused on charcoal. After cleansing by scrubbing with sand and etching with nitric acid, the buttons were again dissolved in nitric acid and the metal was precipitated from solution with ammonium formate. The thoroughly washed product was fused with a blowpipe upon a crucible of the purest

[1] Baxter, THIS JOURNAL, 30, 286 (1908).

[2] See especially Richards and Wells, *Pub. Carnegie Inst.*, No. 28, 16 (1905); THIS JOURNAL, 27, 472.

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lime. Electrolytic deposition with silver nitrate as the electrolyte and with a dissolving anode of the pure silver buttons followed, and the electrolytic crystals were fused in a current of pure hydrogen on a boat of the purest lime. The resulting bars of metal were first cleansed with nitric acid and then were sawed into pieces of a convenient size with a fine jeweler's saw. After the fragments had been etched with nitric acid until free from surface contamination with iron from the saw, they were thoroughly washed with ammonia and pure water, and finally heated to about 300° in a vacuum. The silver was preserved in a desiccator over solid potassium hydroxide.

Pure silver nitrate was prepared by crystallization of the commercial product until free from chloride. That used in analyses 6, 7, 8 and 15 was a portion of material purified by Dr. Grinnell Jones for work upon the atomic weight of phosphorus.[1]

In the preparation of reagents the precautions usual in exact work were taken. The ordinary distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone, through block-tin condensers. Hydrochloric and nitric acids were distilled through quartz condensers, in the case of the hydrochloric acid the first and last running being rejected, in the case of the nitric acid two distillations being carried out, the first third being rejected in each distillation. By careful tests it was shown that nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is nearly free from the latter element.

Quartz or platinum utensils were employed wherever glass would have introduced objectionable impurities, and electrical heaters were used whenever the products of combustion of illuminating gas were to be avoided. In the crystallization of solids centrifugal drainage was always used to assist in the mechanical removal of mother liquor from crystals, except in the fractional crystallization of the neodymium material where it would have been of little assistance.

The Drying of the Neodymium Chloride.

The drying of the neodymium chloride for analysis presented several difficulties. Matignon[2] states that if the chloride is first completely dehydrated and then fused in a current of dry hydrochloric acid gas, the product is completely soluble in water. Our earlier experiments did not confirm this statement, for in several instances salt which apparently had been very completely dried, after fusion in a current of hydrochloric acid gas was found to contain a considerable amount of basic salt. Since, however, material which had been dried at temperatures slightly below the melting point of the anhydrous salt gave ab-

[1] Baxter and Jones, *Proc. Am. Acad.*, 45, 137 (1909); THIS JOURNAL, 31, 298.

[2] *Compt. rend.*, 133, 289 (1901).

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solutely clear solutions, the expedient was adopted of drying the salt for analysis as completely as possible without fusion, with the expectation of determining the water in subsequent experiments. During later experiments for determining the residual water it was found that the preliminary drying had not been effective in the earlier experiments, and that salt which has been dried as for analysis and then fused in a current of hydrochloric acid gas does give a perfectly clear solution. This information was unfortunately acquired too late to be of direct use in preparing the salt for analysis. Since, however, the dried but unfused salt was found to contain a constant very small proportion of moisture, and since a correction was applied for this moisture no appreciable error could have been introduced by the incomplete drying. It is hoped, nevertheless, before long to institute further analyses with material which has been fused.

The apparatus employed in the drying of the neodymium chloride was essentially that used by numerous investigators in this laboratory for the dehydration of chlorides. Hydrochloric acid gas was generated by the action of concentrated sulfuric acid upon concentrated hydrochloric acid, and was dried by passage through five towers about thirty centimeters long and four centimeters in diameter filled with glass beads moistened with concentrated sulfuric acid. Nitrogen was prepared by Wanklyn's method of passing air through a concentrated ammonia solution and then over hot copper. The excess of ammonia was removed and the nitrogen was purified and dried by passing over dilute sulfuric acid, silver nitrate solution, solid caustic potash, concentrated sulfuric acid, and resublimed phosphorus pentoxide. Nitrogen prepared in this way always contains hydrogen,[1] produced by the catalytic decomposition of the excess of ammonia in passing over the hot copper, in quantities which vary with the excess of ammonia and the temperature of the copper, as well as the length of the copper layer and the speed of the gases. The hydrogen could not have had any effect upon the neodymium chloride, however, and was an advantage in preventing the attacking of the platinum boat. Air was purified and dried by reagents similar to those used in the purification of the nitrogen. The hydrochloric acid apparatus was constructed wholly of glass, and the nitrogen and air purifying trains had short rubber connections only at the beginning. Any one of these gases or any desired mixture could be delivered through the tube in which the boat containing the salt was placed. This tube could be heated to constant temperatures in an oven consisting of two superimposed solid aluminium blocks.[2]

[1] Our attention was first called to this fact by Dr. R. C. Wells.

[2] Baxter and Coffin, *Proc. Am. Acad.*, 44, 184 (1909); THIS JOURNAL, 31, 206.

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According to Matignon,[1] at about 105° neodymium chloride loses five of its six molecules of water of crystallization rapidly, while the sixth molecule appears at 160°. We have determined the melting point of the hexahydrated chloride (made from fraction 2931) to be 124°. Thus the drying of the chloride may be caused to take place by a process of double efflorescence, a condition very favorable for the complete elimination of the water. Richards[2] has pointed out that a hydrated salt dried wholly by efflorescence can be freed from moisture much more effectively than one which has been allowed to melt during the dehydration, hence care was taken to keep the temperature below 124° until the greater part of the water had been expelled.

The powdered crystals of neodymium chloride were placed in a platinum boat which had been previously weighed in a weighing bottle, and the boat was heated in a current of mixed nitrogen and hydrochloric acid gases at gradually increasing temperatures. The boat was contained in a hard glass tube which formed part of a "bottling apparatus,"[3] and this in turn was attached to the systems for purifying the various gases. The temperature was kept below 124° until the larger portion of the water had been expelled. Then it was gradually raised to 200°, and finally the salt was heated at about 330° for one hour in a current of pure hydrochloric acid gas. During the heating there was never the slightest appearance of melting. In the first five analyses the final temperature was higher than in the subsequent ones, and was not far below the fusing point of the anhydrous salt. After the tube had been allowed to cool, the hydrochloric acid was displaced by nitrogen and finally by air, and the boat was transferred to the weighing bottle without exposure to moist air by means of the bottling apparatus. After long standing in a desiccator near the balance the boat and contents were weighed.

The Method of Analysis.

In order to dissolve the chloride the boat was first transferred to a large dry Erlenmeyer flask, a column of bulbs was inserted in the neck of the flask and enough water to cover the boat was introduced through the bulbs. These precautions were taken because of the violence of the action of the water upon the finely divided anhydrous salt, in order to avoid both mechanical loss of material and possible evaporation of hydrochloric acid, owing to hydrolysis at the high temperature which results at the moment when the salt comes in contact with water. That the error is not a serious one is evident from the fact that although in the first five analyses the use of the column of bulbs was omitted, yet

[1] *Compt. rend.*, 133, 289 (1901).
[2] *Zeit. physik. Chem.*, 46, 194 (1903).
[3] Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

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the results of these analyses are not markedly different from the others. The solution was allowed to stand in the flask for some time in order to ensure absorption of any volatilized hydrochloric acid. Every specimen of salt dried and dissolved in this way gave a perfectly clear solution.

The solution of the neodymium chloride was diluted to a volume of about one liter with water containing a small amount of nitric acid. Then an equally dilute solution of a very nearly equivalent amount of pure silver nitrate containing nitric acid was added to the solution of the chloride. The glass-stoppered precipitating flask containing the solution was thoroughly shaken and allowed to stand for about twenty-four hours, and then an excess of silver nitrate of about one tenth of a gram was added to complete the precipitation.

After standing until the supernatant liquid was perfectly clear, the precipitate was thoroughly washed, first with dilute silver nitrate solution and then with very dilute nitric acid in the earlier analyses, with pure water in the later ones, and was collected upon a weighed Gooch-Munroe-Neubauer crucible. Then, after the crucible and contents had been dried in an electric air bath at about 150° for eighteen hours, they were weighed.

The moisture retained by the dried silver chloride was estimated in each analysis by determining the loss in weight during the fusion of the dried silver chloride in a weighed porcelain crucible. The weight of silver chloride dissolved in the filtrate and silver nitrate wash-waters was assumed to be 0.00003 gram per liter.[1] That dissolved in the acid or aqueous washing together with the ammonia rinsings of the precipitating flask was determined by comparison with standard solutions in a nephelometer, the usual precautions being taken to secure uniformity of precipitation.[2]

When the ratio of the neodymium chloride to metallic silver was to be determined, a quantity of silver equivalent to the chloride within a very few tenths of a milligram was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. The quantity of silver was adjusted exactly by means of a hundredth normal solution of silver. After the silver solution had been freed from oxides of nitrogen it was diluted to a volume of one liter and was quantitatively added to the chloride solution. The precipitate was caused to settle completely by occasional shaking and standing for several days. Then portions of the mother liquor were tested for excess of silver or chloride by the addition of hundredth normal chloride or silver nitrate solutions, and comparison of the opalescence produced

[1] Richards and Wells, *Pub. Carnegie Inst.*, No. 28, 30 (1905); THIS JOURNAL, 27, 487.

[2] Richards and Wells, *Am. Chem. J.*, 31, 235 (1904); 35, 510 (1906). Richards and Stähler, *Pub. Carnegie Inst.*, No. 69, 20 (1907); THIS JOURNAL, 29, 635.

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in a nephelometer. Deficiencies in either chloride or silver were made up by means of the dilute standard solutions of these substances until finally exactly equivalent amounts of chloride and silver were present in the solution.

In all except the first two titrations the solubility of the silver chloride in the mother liquor was very much decreased by cooling the solution with ice water, a method of increasing the accuracy of nephelometric observation which has been devised recently by Richards and Willard and used successfully in their revision of the atomic weight of lithium.[1]

As soon as equilibrium had been reached in a titration, an excess of one tenth of a gram of silver nitrate was added and the silver chloride was determined gravimetrically as described above. Corrections were, of course, applied for any chloride added in the titration.

The Determination of the Moisture Retained by the Neodymium Chloride.

Although in several cases where hydrated salts have been dried by efflorescence it has been shown that the moisture retained by the salt is negligible in quantity,[2] in the present instance careful experiments were instituted to test this point thoroughly. The direct determination of the water by absorption with phosphorus pentoxide, after fusion of the salt, was complicated in the case of neodymium chloride, since, if the salt is fused in nitrogen, after being dried, hydrochloric acid is liberated, owing to hydrolysis with the residual moisture. Fusion in a current of hydrochloric acid gas is not permissible because of the action of this gas upon the phosphorus pentoxide[3] necessary for the absorption of the water.

Fortunately neodymium chloride is only very slightly volatil at temperatures not far above its fusing point,[4] so that it is possible to estimate the moisture content of the dried salt by fusion in a current of hydrochloric acid gas and determination of the loss in weight. The trace of chloride volatilized during the fusion can then be collected and weighed.

For these experiments a glass tube is obviously unsuited owing to the action of the hydrochloric acid upon the glass at the fusing point of the chloride and consequent vaporization of alkali chloride into the neodymium chloride as well as into the cooler parts of the tube. Hence, in these experiments a quartz tube was substituted for glass. This

[1] *Pub. Carnegie Inst.*, No. 125, 30 (1910); THIS JOURNAL, 32, 32.

[2] Baxter and Coffin, THIS JOURNAL, 28, 1587 (1906); Baxter and Tilley, *Ibid.*, 31, 212 (1901).

[3] Baxter and Hines, THIS JOURNAL, 28, 779 (1906).

[4] Neodymium chloride fuses at 785° and is not volatil at 1000° according to Matignon. *Compt. rend.*, 133, 289 (1901); 140, 1340 (1905).

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tube was apparently not attacked by the hydrochloric acid gas during a long series of experiments.

The exact procedure was as follows: The boat with a maximum charge of neodymium chloride crystals was heated in a current of nitrogen and hydrochloric acid gases, and was bottled and weighed exactly as in preparing the salt for the chloride analyses. After being weighed the boat was replaced in the quartz tube, and when the air had been completely displaced by hydrochloric acid gas, the tube was electrically heated by means of a removable mica sleeve wound with the resistance wire "nichrome," until the salt was fused. The boat was then bottled in dry air a second time and reweighed. In nearly every experiment a barely visible condensation of concentrated hydrochloric acid solution took place in the cool portion beyond the boat.

Weight of $NdCl_3$ g.	Loss in weight during fusion. g.	Percentage loss in weight.
5.36	0.00045	0.0084
6.73	0.00052	0.0077
5.93	0.00050	0.0084
	Average,	0.0082

The loss in weight of the salt found in this way is caused in part by a slight sublimation during the fusion, the magnitude of which was not determined in the first series of experiments. Since the neodymium chloride employed in the moisture determinations was not of so high a grade of purity as that used in the chloride analyses, the volatilized material probably consisted in part of other chlorides. Hence the proportion of moisture calculated from the loss in weight is certainly a maximum. In a second series of experiments, after the fusion of the salt, the sublimate in the quartz tube was dissolved in water and the solution evaporated to dryness in the weighed platinum boat, and after drying at 135° in hydrochloric acid gas the boat was reweighed.[1] The weights thus obtained were subtracted from the loss in weight of the salt found in the same experiment. When the quartz tube was heated alone in hydrochloric acid gas, no sublimate was formed, showing that the volatilized substance did not come from the quartz.

Weight of $NdCl_3$. g.	Loss in weight during fusion. g.	Weight of volatil matter. g.	Per cent. of moisture.
6.24	0.00050	0.00030	0.0032
7.19	0.00052	0.00030	0.0031
		Average,	0.0032

[1] The mosture retained by neodymium chloride at this temperature is only 7.5 per cent. of its weight. A higher temperature was avoided in order that no portion of the residue might volatilize.

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It is to be noted that the percentage loss in weight in the second series of experiments is identical with that of the first series, although the per cent. of moisture is less than half the percentage loss in weight during fusion. The effect upon the atomic weight of neodymium of correcting for the moisture is to lower the atomic weight by eight thousandths of a unit.

The percentage of moisture found is nearly identical in magnitude with that obtained from iodine pentoxide which had been made by efflorescence of iodic acid, 0.0023.[1]

The fused neodymium chloride seemed to be perfectly soluble in water, the probable reason for the better success in these experiments than in the earlier ones being the more efficient drying of the salt before fusion.

The Specific Gravity of Neodymium Chloride.

Although Matignon[2] had already found the density of anhydrous fused neodymium chloride at 18° referred to water at 4° to be 4.195, for the purpose of confirmation this constant was redetermined by displacement of toluene. On account of the difficulty of removing air from porous material the salt was fused for these determinations. The pycnometer employed was one of special form, modified by Baxter and Hines.[3]

The salt was first carefully dried and then finally fused in a current of hydrochloric acid gas in a small platinum boat, as previously described. The boat and contents were then weighed in a small weighing bottle to which they were transferred by means of the bottling apparatus. The salt was next quickly covered with dry toluene, and a special pycnometer stopper was substituted for the ordinary stopper of the weighing bottle. Entangled air was removed by exhaustion in a desiccator and finally the toluene was adjusted to a mark in a capillary outlet tube in the usual way, after the temperature of the system had been carefully adjusted to 25°. In order to avoid evaporation of the toluene through the ground joint of the pycnometer, this was made tight by means of a weighed quantity of sirupy phosphoric acid. The toluene content of the system being known, the displaced toluene could be found. The specific gravity of the toluene at 25° referred to water at 4° was determined in the same pycnometer to be 0.8636, while Jones[4] in earlier experiments with a different pycnometer found the specific gravity of the same sample to be 0.8633.

A part of the difference between this value and Matignon's can be explained by the different temperatures at which the determinations were made.

[1] Baxter and Tilley, THIS JOURNAL, 31, 212 (1909).
[2] *Compt. rend.*, 140, 1340 (1905).
[3] THIS JOURNAL, 31, 222 (1904).
[4] Baxter and Jones, *Proc. Am. Acad.*, 45, 155 (1910); THIS JOURNAL, 31, 314.

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Weight of $NdCl_3$ in vacuum g.	Weight of toluene displaced in vacuum. g.	Specific gravity of $NdCl_3$. 25°/4°.
1.9967	0.4177	4.128
3.6878	0.7700	4.136
3.2569	0.6798	4.137
		Average, 4.134

If the weights are assumed to have the specific gravity at 8.3,[1] Matignon's value for the density leads to a vacuum correction per gram of substance of +0.000141, while the value 4.13 necessitates a correction of +0.000145. The difference amounts to only four ten thousandths of a per cent., which corresponds to a difference of only one thousandth of a unit in the atomic weight of neodymium. Hence it is of no importance which correction is employed.

The following table indicates the corrections for the buoyant effect of the air applied to the weights of the various substances.

	Specific gravity.	Vacuum correction.
Weights	8.3	
Toluene	0.863	+0.00126
$NdCl_3$	4.134	+0.000145
AgCl	5.56	+0.000071
Ag	10.49	—0.000031

All weighings were made on a nearly new balance, Troemner No. 10, which is employed exclusively in atomic weight researches. Weighings were made by substitution for counterpoises as nearly as possible like the objects weighed both in weight and in volume. The weights were carefully standardized to hundredths of a milligram by the method described by Richards.[2]

Results and Discussion.

In order to show that no appreciable error occurred owing either to occlusion by silver chloride or from loss of silver chloride in solution, the ratio between the silver used and the silver chloride obtained has been calculated in the five pairs of analyses for which the data are available.

Analyses.	Ag : AgCl.
8 and 16	0.752663
10 and 17	0.752726
12 and 19	0.752626
13 and 20	0.752686
14 and 21	0.752621
Average,	0.752664

[1] Baxter, *Proc. Am. Acad.*, 42, 209 (1906).

[2] This Journal, 22, 144 (1900).

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Atomic Weight of Neodymium.

Series I. $NdCl_3 : 3\,AgCl$.

Ag = 107.880 Cl = 35.457.

No. of analysis.	Fraction.	Corrected weight of $NdCl_3$ in vacuum. g.	Weight of AgCl in vacuum. g.	Loss on fusion. g.	AgCl dissolved in wash water. g.	AgCl added in titration. g.	Corrected weight of AgCl in vacuum. g.	Ratio $NdCl_3 : 3AgCl$.	Atomic weight of neodymium.
1.....	1302	3.16218	5.42334	0.00030	0.00242		5.42546	0.582841	144.257
2.....	1302	2.93305	5.02969	0.00047	0.00304		5.03226	0.582850	144.262
3.....	1302	2.99149	5.12978	0.00019	0.00236		5.13195	0.582915	144.289
4.....	1302	2.62468	4.50114	0.00030	0.00254		4.50338	0.582825	144.250
							Average,	0.582858	144.265
5.....	1614	2.38439	4.08848	0.00025	0.00241		4.09064	0.582889	144.278
6.....	1614	2.55827	4.38789	0.00029	0.00131		4.38891	0.582894	144.280
7.....	1614	3.59114	6.15981	0.00026	0.00140		6.16095	0.582887	144.277
							Average,	0.582890	144.278
8.....	2923–4	4.27402	7.33208	0.00023	0.00218	0.00200	7.33203	0.582925	144.293
9.....	2926–7–8	4.69459	8.06313	0.00029	0.00160	0.01000	8.05444	0.582857	144.264
10.....	2926–7–8	2.79574	4.80313	0.00025	0.00142	0.00800	4.79630	0.582895	144.280
							Average,	0.582876	144.272
11.....	2932–3	2.59810	4.45553	0.00039	0.00227		4.45741	0.582872	144.270
12.....	2932–3	3.42064	5.87107	0.00021	0.00196	0.00410	5.86872	0.582860	144.265
13.....	2932–3	4.11855	7.06994	0.00018	0.00172	0.00630	7.06518	0.582936	144.298
							Average,	0.582889	144.278
14.....	2936–7	3.95958	6.79583	0.00017	0.00179	0.00400	6.79345	0.582853	144.262
15.....	2936–7	2.71834	4.66295	0.00011	0.00111		4.66395	0.582841	144.257
							Average,	0.582847	144.260
							General average.....	0.582876	144.272

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Atomic Weight of Neodymium.

Series II. $NdCl_3$: 3 Ag.

Ag = 107.880. Cl = 35.457.

Number of analysis.	Fraction.	Corrected weight of $NdCl_3$ in vacuum. g.	Weight of Ag in vacuum. g.	Weight of Ag added. g.	Corrected weight of Ag in vacuum. g.	Ratio $NdCl_3$: 3Ag.	Atomic weight of neodymium.
16	2923–4	4.27402	5.51825	0.00030	5.51855	0.774482	144.283
17	2926–7–8	2.79574	3.60989	0.00041	3.61030	0.774379	144.249
18	2932–3	2.77391	3.58159	0.00037	3.58196	0.774411	144.259
19	2932–3	3.42064	4.41676	0.00019	4.41695	0.774435	144.267
20	2932–3	4.11855	5.31786	0.00000	5.31786	0.774475	144.280
					Average,	0.774440	144.269
21	2936–7	3.95958	5.11284	0.00050	5.11289	0.774431	144.266
22	2936–7	4.64435	5.99649	0.00041	5.99699	0.774447	144.271
					Average,	0.774439	144.269
					General average	0.774437	144.268
					Average of all the results in Series I and II		144.270

Results Averaged by Fractions.

Fraction.	1302.	1614.	2923–4.	2926–7–8.	2932–3.	2936–7.	Average.
$NdCl_3$: 3AgCl	144.265	144.278	144.293	144.272	144.278	144.260	144.274
$NdCl_3$: 3Ag	.....	.....	144.283	144.249	144.269	144.269	144.268
Average of all individual analyses	144.265	144.278	144.288	144.264	144.273	144.264	144.272
Corrected for praseodymium	144.273	144.284	144.288	144.264	144.273	144.268	144.275

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The average ratio of silver to silver chloride is within four thousandths of a per cent. of that obtained by Richards and Wells,[1] 0.752634 : 1.000000.

The results in the preceding tables add further evidence to that already obtained by the spectroscope, that all the samples analyzed were of a high degree of purity. Fraction 2923–4 contained all the rare-earth impurities of higher atomic weight than neodymium which accumulated in sixty-seven series of crystallizations, and actually was found to contain a trace of samarium, while fraction 2936–7 contained more praseodymium, probably not more that 0.1 per cent., than any other fraction of the last series which was analyzed. The first impurity raises the atomic weight and the second lowers it; yet the difference in the average results of these two extreme factions is only 0.024. The fractions 1302 and 1614 gave results differing from those of fractions known to be slightly purer by amounts no larger than the experimental error. When corrected for the proportion of the chief impurity, praseodymium, the results agree satisfactorily for all the samples except fraction 2923–4, which certainly contained an unestimated proportion of samarium.

The results obtained from fractions 1302, 1614 and 2923–4 naturally are less reliable than those obtained from the other three fractions. The corrected average for fractions 2926–7–8, 2932–3, 2936–7, is, however, 144.268, which differs from the corrected average for all six fractions, 144.275, by less than 0.01. It is evident that the value 144.27 can safely be taken to represent with accuracy the atomic weight of the purest material which we have succeeded in preparing. This value is essentially identical with the one chosen by the International Committee upon Atomic Weights, 144.3, and lies midway between the results of Auer von Welsbach and Feit and Przibylla on the one hand and that of Holmberg on the other.

We are indebted particularly to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels, as well as to the Welsbach Light Company for the neodymium material.

Summary.

1. It is emphasized that crystallization in more than one form is advisable for the preparation in a pure state of salts of rare earths.

2. The preparation of a very pure neodymium salt is described.

3. The absorption spectrum of neodymium is described.

4. A method of obtaining anhydrous neodymium chloride is given.

5. The specific gravity of anhydrous neodymium chloride is found to be 4.134 at 25°/4°.

[1] *Pub. Carnegie Inst.*, No. 28 (1905); THIS JOURNAL, 28, 456.

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6. The most probable value of the atomic weight of neodymium is found to be 144.27, if silver is taken at 107.88; with silver at 107.87 neodymium becomes 144.26.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

REVISION OF THE ATOMIC WEIGHT OF CALCIUM.

(SECOND PAPER.)

ANALYSIS OF CALCIUM CHLORIDE.

BY THEODORE WILLIAM RICHARDS AND OTTO HÖNIGSCHMID.

Received November 24, 1910.

In an earlier paper concerning the analysis of calcium bromide[1] it was shown that the atomic weight of calcium is probably not far from 40.070, this being in all likelihood the minimum, if silver is taken as 107.88. Two series of analyses containing each six individual experiments, carried out according to two methods, gave this number as their mean. The present paper contains a description of further work upon this constant, involving now the chloride instead of the bromide of calcium.

The importance of carrying out systematic experiments upon more than one compound is evident. The constant errors due to possible unknown impurities, as well as to possible defects in method, so surround any work of this kind that no worker with much experience is inclined to trust a single method, even although a single good method is worth more than any number of bad ones. The exact analysis of the chloride might add either essential confirmation of the work on the bromide or important evidence concerning possible flaws. Five preliminary experiments upon the chloride carried out at Harvard thirteen years ago had indeed yielded a result which almost although not quite agreed with the figure given above[2]; but this preliminary work was done at a time when considerably less was known about the possible errors in working with chlorides than at present. In any case further work upon the chloride seemed to be imperative.

The present paper concerns the determination of the quantitative relation of metallic silver to pure fused calcium chloride. Both of these substances were weighed with great accuracy, and the end point of the reaction between them was determined in very dilute solution by means of the nephelometer. This method, because of its greater simplicity, is somewhat to be preferred to the weighing of the silver chloride produced from a given amount of calcium chloride. Moreover the preliminary experiments with the chloride had involved this latter process; therefore the comparison with metallic silver would furnish a new ratio, not hitherto investigated.

[1] Richards and Hönigschmid, THIS JOURNAL, 32, 1577 (1910).

[2] Richards, *Ibid.*, 24, 374 (1902); *Z. anorg. Chem.*, 31, 271 (1902).

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We are glad to acknowledge the generous support given this investigation by the Carnegie Institution of Washington.

Preparation of Materials.

Calcium Chloride.—Two different specimens of exceedingly pure calcium carbonate remaining from the preparation of the bromide served as the starting point of the work on the chloride. Repetition of the details is unnecessary; the only impurities which could have been present besides moisture were traces of ammonium nitrate included in the precipitate. Each of these specimens was dissolved in specially purified hydrochloric acid, which had been boiled repeatedly with small additions of permanganate, and then distilled twice in succession with the help of a quartz condenser. The calcium carbonate had been heated in a platinum dish to a temperature high enough to free it from water and ammonia, but traces of nitric acid may have remained; accordingly, the carbonate was dissolved in hydrochloric acid, in a quartz dish, and the chloride was evaporated to dryness. Subsequently it was crystallized three times, each time being freed as completely as possible from mother liquor, by means of the platinum centrifuge. Thus two specimens of calcium chloride were obtained and to them were given the designations 1 and 2, corresponding to the designations of the carbonate from which they were made.

The mother liquors from these two chlorides were collected, concentrated and four times recrystallized. The mixture of the two specimens thus obtained having a purity not far different from samples 1 and 2 was designated sample 3, and served for several analyses.

Silver.—Three preparations of silver were used for this work. Of Sample A the preparation has already been described in the previous paper, and Sample B was made in a similar way by Richards and Willard in their work upon the atomic weight of lithium, already cited. The third, Sample C, was prepared by Dr. C. J. Moore and kindly given to us for this work. Silver residues, consisting of the three silver halides, were reduced with zinc. The metal was washed, dissolved in nitric acid, and precipitated as chloride. This was dissolved in ammonia and again precipitated with nitric acid, and once more reduced by means of sugar solution after very thorough washing. The metal thus obtained was melted (by means of the blast lamp on blocks of lime), etched with nitric acid, and then used as an anode in a dilute silver nitrate solution. A pure silver wire served as a cathode; upon this the silver was deposited in beautiful crystals, and these were carefully washed and melted in a stream of hydrogen in the same way as Samples A and B. The boat of pure lime which served to support the metal was so arranged that the buttons were of various sizes. The pure metal was etched with dilute nitric acid, thoroughly washed and dried in a vacuum at 500°. Pure

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nitric acid and other substances were prepared with the usual precautions adopted in this laboratory.

Melting and Weighing of the Calcium Chloride.

The crystallized chloride, like the bromide, cannot be conveniently dehydrated by heating the hydrated crystals, because a crust forms over the liquefied mass. This greatly hinders the evaporation, which is almost invariably accompanied with projection or spattering of drops. On the other hand, as in the case of the bromide, if calcium chloride is placed in a vacuum desiccator at a temperature below its transition point, 29°, the water leaves the salt with considerable rapidity and the dried skeleton of the crystal can then be heated to 200 or 300° without danger of loss. In the present case a fortnight's standing in a vacuum desiccator over lime in the best vacuum obtainable by means of a Geryk pump was quite enough for preliminary treatment.

The thoroughly effloresced material was further dehydrated and finally fused in an apparatus essentially like that used for the melting of the bromide and almost exactly similar to that used by Richards and Willard for the melting of lithium chloride.[1] The calcium chloride was contained in a platinum boat enclosed in a wide quartz tube connected with the familiar Harvard "bottling apparatus," and in this position was gradually brought by means of electrical heating to the temperature of 400°, in a current of nitrogen. After an hour the air in the tube had been displaced, and the salt was almost wholly free from water. Turning the 3-way cock then admitted dry hydrochloric acid gas; and as soon as all the nitrogen had been displaced the temperature of the chloride was raised to its melting point, about 800°. For fifteen minutes the fusion was maintained in the current of acid gas; then this gas was displaced by nitrogen, and the fusion was continued until the greater part of the hydrogen chloride had been given out by the inert element. The product was then allowed to cool rapidly in nitrogen.

During the cooling a hitherto unnoticed phenomenon was observed. As the temperature decreased, the perfectly clear glassy solid, which was at first formed in the boat, was flecked with small white spots. These were caused by the shattering of the glassy chloride as it crystallized, sometimes almost explosively, at the lower temperature; and they gradually spread over the whole surface. Occasionally some particles of the salt were thrown out of the boat during this process. The effort was made to prevent the change by cooling as quickly as possible. This device was unsuccessful, but we found that the transition could be prevented by heating the salt for a long time in nitrogen. From this fact the conclusion may be drawn either that traces of hydrochloric acid are dissolved by the fused salt, and that these traces hasten the crystallization, or else that

[1] Richards and Willard, THIS JOURNAL, 32, 25 (1910).

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the traces of alkali formed by long ignition in nitrogen retard the crystallization. The transition phenomenon is accompanied by considerable increase in volume; in one case, indeed, a thin platinum boat was so much increased in diameter by the expanding salt as to make it incapable of admission into its weighing glass—a mishap which naturally caused the loss of that experiment.

After the chloride had been completely cooled and the apparatus again filled with pure dry air, the boat and its contents were pushed into the weighing bottle and allowed to stand at least six hours in a desiccator in the neighborhood of the balance. It was then weighed in the usual fashion by substitution.

The platinum boat was attacked somewhat more strongly by hydrochloric acid than by hydrobromic acid. Nevertheless, since the average loss was only 0.08 milligram in a single experiment, and since any platinum which had been dissolved probably reverted to the condition of metal in the salt during its fusion in a neutral atmosphere, this complication may be left entirely out of account. The original weight of the boat was taken in each case as the true one.

The experiments with the bromide had already shown us that with a salt as easily decomposed as calcium chloride, it is by no means easy to obtain an exactly neutral product. Accordingly each specimen of fused calcium chloride was dissolved in a small amount of water and then titrated with $^1/_{100}$ normal nitric acid or caustic potash, using methyl red as an indicator. The departures from neutrality were so slight that they scarcely could have been observed and could not have been accurately estimated without comparison with a standard solution of calcium chloride known to be neutral. This latter was prepared by crystallizing moderately pure calcium chloride, faintly acid, four times from the purest water with thorough centrifugal treatment and all precautions. An equal quantity of this certainly neutral salt was dissolved in precisely the same amount of water as was used for the sample to be tested, and to each was added the same quantity of methyl red. In most cases the solution of the melted chloride was thus found to be slightly acid, and only when the product had been fused in dry nitrogen for some time did an alkaline reaction appear. Whether the lack of chlorine evidenced by the alkaline reaction was caused by traces of oxygen or water in the nitrogen or by a reduction to subchloride cannot be absolutely proved; but the former is by far the most likely assumption, therefore it was made in calculation of the results. In this way it was found that the eighth, tenth, and eleventh specimens were precisely neutral, as nearly as this testing could show it. The sixth, seventh, and ninth were slightly acid, requiring 0.10, 0.30 and 0.20 milliliters of $^1/_{100}$ alkali respectively, whereas the twelfth sample of calcium chloride was alkaline, needing 0.70 ml.

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of $^1/_{100}$ normal acid for its neutralization. In order to correct for these slight deviations from neutrality a small correction was added to or subtracted from the weight of the calcium chloride according as the calcium was lacking (in slightly acid specimens) or calcium oxide was present as an impurity (in the alkaline specimen). The actual amounts of the corrections in analyses 6, 7, 9 and 12 amounted respectively to + 0.00002, +0.00006, +0.00004 and —0.00020 gram.

It is interesting to note that the sum of all these corrections is a negligible quantity. Their effect is only to improve slightly the agreement of the results. Thus, on the average, the calcium chloride was neutral. This is especially important in its bearing upon other cases, because occasionally, for example in the case of zinc bromide,[1] indicators give results so unsatisfactory that no clue can be gained as to the neutrality of the fused salt after it has been dissolved. Evidently the amount of acid gas dissolved by the fused salt at a bright red heat is almost negligible, even when the acid gas is present under a full atmosphere's pressure.

The weighings were made upon the same balance and in the same way as has been already described. For the determination of the correction to vacuum of the calcium chloride, it was necessary to determin the weight of air displaced by a given weight of this substance.

The density of fused calcium chloride was determined in the pycnometer devised by Baxter[2] for salts of this kind. Toluene having a specific gravity 0.8630 at 25°, compared with water at 25° (that is to say, weighing 0.8605 gram per cubic centimeter), was used as the liquid to be displaced. Two pairs of experiments were made. In the first pair 4.8462 grams in vacuum of fused calcium chloride displaced 1.9417 grams in vacuum of toluene, and in another pair 4.1223 grams of calcium chloride displaced 1.6447 grams of toluene, the temperature being 25° as before. These two results correspond respectively to values for the density of calcium chloride of 2.148 and 2.156, the mean being 2.152. This value is used in calculating the corrections of the vacuum standard. Because the specific gravity of the gilded brass weights was 8.3, the following vacuum corrections per gram were applied.

	Density.	Vacuum correction.
Silver	10.49	—0.000030
Silver chloride	5.56	+0.000071
Calcium chloride	2.15	+0.000415

Precipitation and Gravimetric Titration.

The weight of silver supposed to be exactly equivalent to each fused and weighed portion of calcium chloride was dissolved with all ordinary precautions in nitric acid. After dilution the liquid was heated, in order

[1] Richards and Rogers, *Proceedings Am. Acad.*, 31, 158 (1895).
[2] Baxter and Hines, *Am. Chem. J.*, 31, 221 (1904).

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to expel nitrous vapors, and then diluted further to a liter. The chloride solution also, after being tested for its neutrality, was diluted to a liter in the three-liter Erlenmeyer flask which had served originally for its dissolving. The silver solution was added little by little to the chloride solution in the dark room; and the flask was then closed and the mixture shaken for a short time in order to mix thoroughly the two solutions. Violent shaking was not practised, because this causes the precipitate to cohere, and prevents the washing out of included chloride or silver. On the following morning the mixture was shaken energetically for about fifteen minutes, and then packed in ice in order to diminish the solubility of silver chloride by lowering the temperature and thus to increase the accuracy of the determination of the end point. The question as to whether silver or chloride was in excess in the supernatant liquid was then determined by means of the nephelometer in precisely the same way as had been used in the already often quoted work on the atomic weight of lithium, where the details are to be found. The test was made only after the chloride solution had remained for twenty-four hours in the cooling bath. Seven determinations gave the following results:

RATIO OF CALCIUM BROMIDE TO SILVER—FINAL CALCULATIONS.

No. of exp.	Sample of calcium chloride.	Sample of silver.	Corrected weight of calcium chloride in vacuum.	Weight of silver in vacuum.	$2Ag : CaCl_2 =$ 100 : x.	Atomic weight of calcium.
VI	I	A	4.60350	8.94908	0.514410	40.075
VII	II	B	4.82401	9.37780	0.514407	40.074
VIII	II	C	4.81846	9.36688	0.514415	40.076
IX	II	C	5.29799	10.29911	0.514412	40.076
X	III	C	5.40550	10.50832	0.514402	40.073
XI	III	C	5.24539	10.19715	0.514398	40.073
XII	III	C	5.34110	10.38328	0.514394	40.072
			35.53595	69.08162	0.5144054	40.074

It is to be noticed that the three samples of silver gave results essentially identical, and that the three specimens of calcium chloride were also practically alike, within the limit of error in experimentation. The quantity of material used, although not differing greatly in the individual experiments, seems to have produced no noticeable effect on the results. It is worthy of remark that the series of determinations was an uninterrupted one, no experiments having been rejected from it.

These analyses thus lead to the number 40.074 for the atomic weight of calcium, if silver is taken as 107.88 and chlorine as 35.457. The probable error of this series of results is smaller than that of either of the two series with bromide, being only 0.0004. The maximum deviation from the mean is only 0.002 in the atomic weight of calcium, which corresponds to about 1 part of calcium chloride in 55,000. The agreement is there-

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fore as good as could be expected in work of this kind. The reason for the improvement over the previous series is undoubtedly to be found in the increase of experience with which this last problem was attacked. The knowledge gained in earlier work was of great service in the later determinations.

The Atomic Weight of Calcium.

Four series of determinations concerning the atomic weight of calcium have been carried out in the Harvard laboratory. The first series, executed in 1897 and 1898, claimed to be nothing more than a preliminary treatment of the subject, and was undoubtedly subject to several minor possibilities of error which modern knowledge could have eliminated. The present authors in their recent paper on the analysis of calcium bromide contributed the next two series, and the analysis which has just been described completes the list. The results of these four series with their respective "probable errors" are entered in the following table:

From the ratio $2AgCl:CaCl_2$	$Ca = 40.085(\pm 0.0011)$
From the ratio $2AgBr:CaBr_2$	$Ca = 40.070(\pm 0.0007)$
From the ratio $2Ag:CaBr_2$	$Ca = 40.070(\pm 0.0007)$
From the ratio $2Ag:CaCl_2$	$Ca = 40.074(\pm 0.0004)$
Average for the atomic weight of calcium	$Ca = 40.075$

This average, 40.075, is almost exactly identical with the last of the four series, and may be taken as the atomic weight of calcium, if silver = 107.88 and chlorine = 35.457. Possibly silver is really as low as 107.87; if this is the case, the atomic weight of calcium would become 40.072. It would appear that Hinrichsen's value, 40.142,[1] is in all likelihood distinctly too high. A repetition of the first, slightly divergent series, given in the above table, has already been begun; but the work has been interrupted by the necessary departure of one of us for Europe. It will be continued in the near future.

Summary.

The most important results recounted in the present paper are as follows:

Pure calcium chloride was prepared by dissolving very pure carbonate in very pure hydrochloric acid by crystallization of the product. Three samples gave consistent results, showing the material to have been pure.

Fused calcium chloride was found to suffer transition into a more bulky form on cooling, if traces of hydrochloric acid are present. The glassy fused salt, obtained by the fusion of a neutral or slightly alkaline salt, was found to have the density 2.15 at 25°.

By gravimetric titration 35.53595 grams of fused neutral calcium chloride were found to require 69.08162 grams of silver in seven consecutive ex-

[1] *Z. physik. Chem.*, **39**, 311 (1901).

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periments, corresponding to an atomic weight for calcium of 40.074, if silver is 107. 88.

This value equals almost exactly the average of all the Harvard work upon the subject, 40.075, and may be taken for the present as the most probable atomic weight of calcium.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

A DETERMINATION OF THE RATIO BETWEEN CHLORINE AND BROMINE AND SODIUM.

BY JACOB S. GOLDBAUM.

Received November 26, 1910.

Introduction.

Before the National Academy of Sciences, Wolcott Gibbs, in 1880, first suggested the use of mercury as cathode in electro-analysis. His experiments, although purely qualitative, were sufficient to indicate the correctness of the principle involved. The subsequent development of the mercury cathode cell in metal determinations furnishes an important chapter in the history of analytical chemistry, but it is to its extension into the domain of anion estimation that especial attention is now directed.

Vortmann[1] and later Specketer[2] had published brief accounts of halogen fixation, but the activities of Edgar F. Smith and his students in the use of an attackable silver anode with a mercury cathode, made for sure and steady advance in this phase of our science. Within the last decade much has been published of results obtained in this laboratory in the analysis of alkali and alkaline earth salts, with particular emphasis upon the halides of these metals. The advent of the "double cup" as devised by Hildebrand was important and timely. By its use many analyses and separations of decided interest have been effected, as is evident by reference to the work of Hildebrand,[3] McCutcheon,[4] McCutcheon and Smith,[5] Lukens and Smith,[6] Kollock and Smith,[7] and Goldbaum and Smith.[8]

Extreme accuracy has always been a feature of the values obtained in the papers mentioned above. It seems, however, that in the hands of other investigators, difficulty in duplicating results is being encountered

[1] *Elektrochem. Z.*, 1, 137.
[2] *Z. für Elektrochem.*, 4, 539.
[3] THIS JOURNAL, 29, 447.
[4] *Ibid.*, 29, 1445.
[5] *Ibid.*, 29, 1460.
[6] *Ibid.*, 29, 1455.
[7] *Proc. Am. Philos. Soc.*, 46, 341.
[8] THIS JOURNAL, 30, 1705; 31, 900; and 32, 1468.

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from time to time. In the manipulation of the method there are many points of detail that heretofore have not been fully discussed. These have been more thoroughly studied in the present work. It is hoped that with the publication of this paper the mode of procedure will be made clear and the reliability of the method established beyond further doubt. This paper aims to indicate the application of electrolysis in general, and of the method in particular, to the highly exacting field of atomic weight work, itself the severest test to which any analytical procedure can be subjected. Full appreciation is held of the remarkably trustworthy character of the present values of the atomic weights of the halogen elements. It was, therefore, not in a spirit of revision, but rather with the idea of attacking the problem from an entirely different and novel standpoint that this work was undertaken.

Fundamentally the principle employed is extremely simple. An aqueous solution of common salt, for example, is electrolyzed with a weighed silver anode and mercury cathode. Sodium as cation forms an amalgam, chlorine attaches itself firmly to the silver, and the increase in weight of the anode represents the halogen content of the salt. In his monumental work on atomic weights, Berzelius always laid especial stress on "simplicity of analysis or synthesis of the simplest compounds." This dictum furnishes the keynote of the present investigation.

The many publications of atomic weight values of chlorine and bromine made within quite recent years contain admirable résumés of all methods heretofore employed, together with a listing of the results obtained by various investigators. It is hence deemed unnecessary to adopt a like procedure in this paper, and reference to "A Recalculation of the Atomic Weights," by F. W. Clarke,[1] is recommended.

Experimental Part.

Apparatus.—The electrolytic cell resembles in principle that used in the Castner-Kellner process for the decomposition of salt. It consists of a glass crystallizing dish 16 cm. in diameter, 6 cm. high, in which is placed a bottomless beaker 5 cm. high and 7 cm. in diameter. An equilateral triangle of thin glass rod with one angle left open acts as a spring to hold the beaker firmly in the center of the outer dish and likewise permits of easy adjustment of the lower rim of the beaker to within about 4 mm. from the bottom of the crystallizing dish. A layer of mercury 1 cm. in thickness (depth) placed in this immediately forms a two-compartment cell with the mercury as a seal. Extending around the inside of the outer compartment, about 1 cm. above the level of the mercury, is a ring of platinum wire holding a prong of the same metal which dips in the mercury. A stout platinum wire, partially encased in glass and held in position by a support clamped to a glass stand, serves as cathode connection for the

[1] Smithsonian Institution Publication, 1910.

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mercury with the negative pole of the circuit. The cell is covered with two semi-circular, well-fitting glass plates. The center of each plate is notched and ground to admit the anode when the cover glasses are in position. Actual contact of the ground glass with the platinum anode is prevented by a protective platinum foil.

Special attention must be paid to the form of anode used. As finally adopted this consists of three circular discs of platinum gauze 5 cm. in diameter and 30 meshes per cm., the circumference of each being slightly fused. They are mounted 8 mm. apart on a platinum rod 1 mm. in diameter and 10 cm. long which passes through the centers of the discs perpendicular to them. The silver plating of the anode will be discussed later. Rotation of the anode is accomplished by fastening it into the shaft of the special kind of motor used for all rotating work in this laboratory.[1] The chuck of the shaft with which the anode came in contact is lined with new platinum foil. The shaft of the motor is connected by ordinary annunciator wire to the positive pole of the battery.

A Weston milliammeter, a Weston voltmeter (graduated to 0.5 v.) and a very efficient Ward-Leonard rheostat are placed in the circuit. The current is derived from a battery of ordinary storage cells.

An electric oven for drying the anode was constructed as follows: Two ordinary iron tripods were fastened bottom to bottom to form a hollow cylinder 22 cm. long and 8 cm. in diameter. "Nichrome" ribbon, $^1/_{16}$ inch wide, 0.0035 inch thick, with a resistance of 2 ohms per foot, was then wound round the asbestos-insulated tripod rods, and the cylinder, with suitable precautions, covered with previously ignited sheets of asbestos. The whole was subsequently placed in a wooden box 28 cm. high and 20 cm. square. On the bottom of the box were four stout corks on which rested a square of asbestos board. The oven was placed on this, and the sides of the box tightly packed with a mixture of plaster of Paris and calcined magnesia. The bottom of the oven proper was covered with a sheet of ignited muscovite and the interior space of the oven protected from the "nichrome" wire by sheets of the same material. Mica likewise formed the cover of the heating device. The oven had a resistance of 60.0 ohms, so that when connected with the ordinary lighting circuit of 110 volts d. c., it gave a temperature suitable for the purpose. This temperature was, of course, cumulative, and in the course of two hours rose steadily to 400°. The insulation served so well that the encasing wooden box was at all times comfortable to the touch. By means of an ordinary screw clamp held on a retort stand, the anode may be lowered into the clean interior of the oven. New platinum foil protected the rod of the anode from the iron screw clamp.

[1] See Smith's "Electro-Analysis," 4th ed., p. 58. The motor used was of the type listed by Greiner and Friederichs as No. 2159.

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A nephelometer as devised and described by Richards and Wells[1] served to determine the amount of dissolved silver halide.

The balance used was of an excellent Troemner design. It was kept in a room isolated from the rest of the laboratory. Successive weighings on it of the same object gave concordance to within 0.03 mg. The weights used were of exceptionally good make, the corrections as applied from the calibration according to the method of Richards[2] being quite small.

Preparation of Pure Materials.

Water.—The distilled water of the laboratory, on examination, contained no chlorides. Traces of organic matter present were destroyed by redistillation from a weakly alkaline permanganate solution, using a block-tin condenser. The first part of the distillate was rejected and the subsequent portions collected in Jena flasks. This water was then again distilled just as needed and was never in contact with the glass for more than twenty-four hours before use.

Sodium Chloride.—Richards and Wells[3] have conclusively shown that the preparation of pure sodium chloride is comparatively easy. The sodium chloride used in this work was obtained from the J. T. Baker Company and was of exceptionally high grade. It was dissolved in pure water and saturated with HCl gas (made from the purest commercial hydrochloric acid and pure concentrated sulfuric acid). The crystals of sodium chloride were then filtered and separated from the mother liquor by centrifugal drainage, using a very efficient home-made centrifuge. They were again dissolved and the entire operation twice repeated. After centrifuging on a large platinum cone, the salt was crystallized four times from platinum and then the dry material was fused in platinum, with the aid of a blast lamp, the products of combustion being suitably deflected. The clear, colorless salt was removed in lumps about the size of a pea and preserved in weighing bottles with well-fitting stoppers.

Sodium Bromide.—The purest bromide furnished by the J. T. Baker Chem. Co. was used as the source of raw material. On careful examination it was found to be free of sulfates, phosphates, carbonates, bromates and iodides, and to contain but a faint trace of chloride. A comparatively large amount of suspended iron was found. This was easily removed by filtration. The filtrate was colorless and free of iron. The sodium bromide from it was recrystallized in platinum six times, each time with efficient centrifugal drainage. Examination at this point failed to reveal any chloride, and the colorless crystals were then recrystallized eight more times from pure water. The salt was now regarded as pure.

It was fused in platinum, and while quite hot was removed from the

[1] *Am. Chem. J.*, 31, 235.
[2] THIS JOURNAL, 22, 144.
[3] *Ibid.*, 27, 459.

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crucible and quickly placed in very warm, dry weighing bottles. Absolutely clear, colorless, brilliant lumps of bromide, somewhat larger than the size of a pea, were obtained and preserved. The hygroscopic nature of sodium bromide necessitated this procedure and the clarity of the lumps of bromide was an indication of its sufficiency.

Silver Nitrate.—The purest silver nitrate obtainable was recrystallized three times in platinum. This was regarded as sufficient for nephelometric work, since values obtained by its use were solely relative.

Nitric Acid.—This was kindly furnished by Dr. W. H. Chapin, who had purified it for his work on the "Atomic Weight of Tantalum." It was entirely free of chlorides.

Ammonium Oxalate.—The colorless crystals of commerce were dissolved in pure water and recrystallized twice.

Ammonia Water.—Ordinary ammonia water was heated and the vapors absorbed in pure water.

Mercury.—Ordinary distilled mercury of commerce was thoroughly washed with potassium dichromate and sulfuric acid, then dried and doubly distilled in Hulett and Minchin's glass distilling apparatus.[1]

Preparation of the Silver Anode.—In the previously published work on anion determinations with the double cup and silver anode, the anode was prepared by plating the gauze discs in a bath of $KAg(CN)_2$ under a voltage of five and an amperage of one. The anode was then washed with water, dried and gently heated, after which it was ready for a determination. Examination by the writer showed that with this procedure there was still some possibility of enclosed cyanide, and so the expedient of dipping the plated gauze in dilute HCl was tried. The HCl formed KCl, which was easily washed out with distilled water. The gauze was then heated to incipient redness and was ready for weighing. Repeated tests showed no trace of soluble matter. The weighed anode could be immersed in boiling water, and re-ignited, without showing any loss in weight, and since after electrolysis the weight of the halogen is determined directly by difference, the above method of preparing the anode plate was obviously satisfactory. However, for the final work in this investigation, recourse was had to the double oxalate of silver and ammonia electrolyte. This was done only because the silver from such a bath was of a more porous character, and hence presented greater surface to the action of the ionic halogen during the electrolysis. The platinum gauze was made the cathode in the oxalate electrolyte, and with the use of a clean platinum rod as anode, a current of 1 ampere at 1.5 volts was sent through the solution. The gauze rotated at about 200 r. p. m. This low current admits of a close, coherent coating on the platinum. It was then gradually increased to four amperes and an extremely heavy porous deposit of silver

[1] *Phys. Review*, 21, 388.

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finally obtained. The proper plating of the gauze requires constant attention for about five hours, because the gas bubbles evolved during the electrolysis collect on the gauzes, act as non-conducting cushions and thus prevent an even coating. The gauze must, therefore, be lifted out of the bath from time to time in order to break the bubbles and hence insure a satisfactory deposit. This deposit is then dipped in dilute HCl and very thoroughly washed with pure water, after which it is heated in the Bunsen flame to incipient redness, cooled in a desiccator and weighed. Repeated ignition with subsequent immersion in water showed no change in weight. This method of preparing the silver anode is therefore adequate.

Mode of Procedure.—Since pure fused chloride of sodium is perfectly stable, its weighing was a very simple matter. The lumps of salt for each determination were transferred from a weighing bottle into a small weighed beaker and the increase in weight of the latter observed, of course using an almost identical beaker for a counterpoise. The weighed beaker containing salt was then carried in a desiccator to the electrolytic cell.

Fused sodium bromide is, however, hygroscopic; and a variation in the above procedure was therefore adopted. The bromide was contained in an exceedingly well-ground weighing bottle, and was weighed against a similar bottle containing bromide. The stopper of the bottle was then removed, about the required amount of salt shaken out into a clean beaker, and the stopper replaced, after which the bottle was ready to be reweighed, the decrease in its weight, of course, representing the apparent weight of the salt used. The operation of removal of salt never consumed over fifteen seconds and the glass was handled through linen gloves. The construction of the stopper of the weighing bottle was such that there was no possibility of loss of bromide in transference. When clear, fused masses of sodium bromide are exposed to the action of ordinary air for even forty-five seconds, the surface becomes clouded and the transparence is lost. Investigation of the increase in weight of the hygroscopic bromide when exposed to the air in the balance case gave the following results: Five grams of bromide were carefully weighed in a closed weighing bottle, the stopper was then removed and the increase in weight noted. In one minute no increase was observed; in three minutes 0.03 mg.; in five minutes 0.06 mg.; in ten minutes 0.13 mg. It is quite obvious that in an actual determination there was no likelihood of error in the weight of the sodium bromide, because of the fifteen seconds or less during which the weighing bottle was open. Furthermore, each successive quantity of sodium bromide removed from the weighing bottle was as brilliant in appearance as the very first taken out.

All weighings were made by substitution. Since the counterpoise was always almost exactly similar to the object weighed, the weights required were never large in amount, and thus errors due to atmospheric

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conditions were greatly minimized. All weighings were, of course, reduced to a vacuum standard, with a consideration of density at 20°.

In the inner compartment of the double cup was placed the salt under analysis. The total dilution never exceeded 65 cc. The weighed, silver-plated anode supported in the platinum-protected chuck of the motor shaft was placed centrically in the inner beaker. The lowest gauze was about 1 cm. above the surface of the mercury. About 5 cc. of a saturated aqueous solution of common salt was then put in the outer compartment and this was diluted with water to about 200 cc. The circle of thin platinum wire was thus completely covered. The rod of platinum serving as cathode connection with the mercury was then put in position and the cover glasses replaced. The anode was rotated at a speed of 200 r. p. m. and the current applied. Decomposition of the salt was instantly visible. The anode darkened because of silver halide. The sodium passed into the mercury as amalgam and was decomposed in the outer cell. This oxidation was greatly facilitated by the introduction of the circle of platinum described, for, in reality, a secondary cell entirely independent of the main electrolytic circuit was established. In this, the elements were amalgam, platinum and the solution of sodium chloride. The purpose of the sodium chloride introduced into the outer compartment is thus to act as a conducting medium at the beginning of the decomposition. Hydrogen bubbles "break" from the platinum wire in a continuous steady stream until the end of the electrolysis.

During the progress of the electrolysis the amperage gradually decreases because of the removal of salt from the inner cell. When the ammeter needle has fallen to below 0.03 amp. the current is interrupted. The anode is raised from the cell, is thoroughly washed with pure water, dried in the electric oven, cooled in a desiccator and weighed. Treatment of the liquid remaining in the inner cup will be described later.

Previous analyses made in the double cup were of quantities of salt rarely exceeding 0.15 gram, and excellent results were obtained, if no decomposition of amalgam occurred in the inner cup. Quite evidently such decomposition would give rise to the formation of sodium hydroxide which would undergo electrolysis with the consequent deposition of silver oxide on the anode. This contaminates the silver chloride alone desired and vitiates the value of the increase in weight of the anode. One cannot foretell just when decomposition of amalgam in the inner cup will or will not take place. Even working with the most scrupulous cleanliness does not necessarily insure complete absence of decomposition in the inner cell, although under such conditions the secondary decomposition would be minimized. This secondary electrolysis is therefore possible and quite likely, and to this cause may, in part, be attributed irregular values occasionally obtained heretofore. Silver oxide, however,

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decomposes at 250° with the liberation of oxygen, whereas silver chloride is stable at a much higher temperature. Thus if the anode after electrolysis, containing AgCl contaminated with Ag_2O, be heated to above 250° the oxide is decomposed, and the anode consists substantially of silver and silver chloride exactly as is desired. This condition was effectually brought about by recourse to the electric oven described above. The temperature ranged from 330 to 400°, and was thus quite sufficient to decompose the oxide. It is noteworthy that the oxide appears on the anode only near the end of the electrolysis and after practically all of the sodium chloride has been decomposed. (Its decidedly brown tinge distinguishes it from the bluish black chloride.) It is thus a superficial formation, and hence can be easily and completely decomposed. It is readily seen that with the use of the drying oven at elevated temperatures, the old bugbear of concomitant oxide formation on the anode is entirely dispelled.

Quite naturally larger quantities than 0.1 g. of material are necessary for atomic weight work, and on increasing this amount considerable difficulty was encountered. With the use of over a gram of salt in solution and an initial voltage of 3.5 the increasing resistance in the cell caused the pressure to rise of itself to 6.5 volts. Complete decomposition of the salt occurred, but a black scum invariably appeared on the surface of the liquid in the inner cup. This black scum was identical with small quantities of a loosely adherent deposit on the silver anode. Examination proved it to be oxide of silver. Quantitative determinations of halogen content under such conditions were, of course, absurd. Continued experimentation led to the adoption and maintenance of a low voltage as a means of preventing the formation of the loose oxide. A voltage of 3.5, kept constant throughout the electrolysis, insured a perfectly adherent deposit. And still the values of halogen obtained were very low. Trial after trial was made with varying conditions, but with no apparent advance.

All this work was done with a "six-decker" platinum gauze especially devised to pick up larger quantities of anions. Examination of the silver plate under a lens led to the discovery of a non-uniform coating, indeed minute spaces of platinum were exposed. Here, then, might be a reason for the low values obtained. If platinum is made the anode in a solution of sodium chloride, some NaClO and $NaClO_3$ are formed, lost, and quantitative retention of halogen as halide is impossible. The nature of the six-gauzed anode used prevented the deposition of a thick adherent plate of silver. The wires of each gauze were too fine in diameter, the gauze was too fine in mesh and the gauzes themselves were too close together. Thus, in attempting the plating of a very heavy deposit the meshes would be closed up, giving even less anodic surface and defeating

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the original purpose of the many-disc electrode. A triple-disc anode, made and prepared as described above, was finally adopted. The proper preparation of the silver anode is most essential to the success of each determination. At no time during the electrolysis must the anion be permitted to come in contact with the platinum. If only small amounts of halide are used, then a comparatively thin coating of silver suffices to retain all the halogen. But in the case of much larger quantities great care must be taken to procure a uniform silver plate of considerable thickness, so that as the chloride ion, for example, converts the surface silver to halide and works its way to the core of the deposit, there should be sufficient silver at all times to protect the platinum base. If the deposit is not uniformly thick, it is readily seen that at the places of this deposit the ionic halogen will soon meet the platinum, even though there be sufficient silver in bulk on the rest of the gauze; and when the platinum becomes the anode, then the very disturbing secondary formations arise. It is very likely that this phenomenon is the chief cause of uncertain values in anion estimations obtained occasionally by various investigators. Emphasis must be laid on the necessity of a satisfactory silver plate. In the present work a deposit of 10 to 15 grams of silver generally obtained. The use of a pure silver anode is, of course, ideal. A three-disc pure silver anode, of the same dimensions as the platinum gauze anode, with sand-blasted and perforated surface, was later used for several determinations and gave excellent satisfaction.

A peculiar phenomenon noted in the course of this work was the appearance, after drying in the oven, of a dark, purplish "sublimate" on the silver-plated rod of the platinum anode, at a place just below the upper limit of the silver coating. Continued heating of the anode showed no loss in weight. Indeed, direct ignition of the "sublimate" had no effect. Since constant weight was obtained, the first thought of a volatil chloride or subchloride of silver, had to be laid aside. It was then believed that the electrolyte was, to a slight degree, drawn up the anode rod by capillarity. This would explain the presence of the apparent sublimate which, on solution in potassium cyanide and reprecipitation by nitric acid, proved itself to be a chloride of silver. The expedient of forming a very coarse deposit of metallic silver immediately above the gauzes proved the correctness of the capillarity assumption. The spongy, though perfectly adherent, deposit really acted as a sponge, and prevented the electrolyte's creeping up the rod and eventually coming in contact with the platinum above.

Silver chloride is, to a slight degree, soluble in water, and so account must be taken of the silver chloride present in the inner-cup liquid after electrolysis. This was done by precipitation of the dissolved chloride with an excess of silver nitrate in the presence of nitric acid and deter-

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mination of the turbidity thus produced by means of a nephelometer.[1] In addition to the dissolved silver chloride, there was also some sodium hydroxide, due to decomposition of amalgam in the inner cup. This had no effect on the nephelometric work, since the silver oxide formed when silver nitrate is added to the inner-cup solution is completely dissolved by the nitric acid added to catalyze the formation of the chloride opalescence. The determination of the silver chloride in solution was carried out as follows:

A standard solution of pure sodium chloride was prepared by dissolving 0.0414 gram NaCl in 250 cc. water. This was solution A. One cc. of it was equivalent to 0.0001 gram Cl. Solution B, 250 cc. in volume, was then made by diluting one cc. of solution A with pure water. A solution of silver nitrate was prepared by dissolving 10 grams silver nitrate in 250 cc. pure water. A 1 : 10 aqueous solution of nitric acid was likewise at hand.

The liquid remaining in the inner cup (never more than 70 cc. in vol.) was pipetted into a calibrated 250 cc. flask, and the inner cup was washed six times with small amounts of pure water, pipetting each washing into the flask. The original wash waters obtained in washing the anode after removal from the inner cup were then added to the contents of the flask and the whole made up to the mark with pure water. These 250 cc. therefore contained all the dissolved silver chloride and since the volume was identical with that of solution B, a direct comparison of the halide content of the two solutions could be made. To this end, one cc. of the silver nitrate solution and one cc. of the nitric acid were added to each of two 6-inch test tubes. One tube was then filled with the solution to be examined, the other with the solution B of known strength. The solutions were thoroughly agitated with clean glass rods and placed in the nephelometer. Constant reading was had after a lapse of fifteen minutes. The ratios of the respective turbidities furnished a direct determination of the halide present in the test solution. For example, if the nephelometric ratio was as 8 is to 4, *i. e.*, the reading of the tube containing the standard was 8.0, whereas the reading of the test solution gave 4.0, then, according to the scale of the instrument, there was twice as much turbidity in the test as in the standard, and consequently twice as much halide.

Although the solubility of silver chloride in water varies, it is less than 2 mg. per liter, so that if the 65 cc. of solution in the inner cup were saturated with AgCl there could only be about 0.1 mg. of the salt in solution; hence an accuracy of only 10 per cent. in the nephelometer would be quite sufficient for the purpose. However, the nephelometer admits of much greater precision, and hence permitted the following variation

[1] *Am. Chem. J.*, 31, 235.

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in the electrolytic procedure. Instead of conducting an electrolysis to the complete analysis of the sodium chloride, the current was interrupted, while traces of undecomposed salt still remained, and these traces were nephelometrically determined, using the same procedure just described. It was a source of great satisfaction that, with the widely varying amounts of chloride determined by the nephelometer, the total halogen obtained gave uniform atomic weight figures. The identical method of nephelometric tests was used in the bromine estimations.

All electrolyses heretofore made with the double cup were conducted in the presence of sunlight or artificial yellow light, and no effort was put forth to prevent the coloration of the silver halide as formed. It seemed desirable in the present work to carry out several analyses of sodium chloride and of sodium bromide in a dark room and to note any variation in effect. Three experiments were accordingly made at night, in complete darkness, except for the occasional use of a red lamp to illuminate the measuring instruments. The dried anode, holding supposedly pure undecomposed silver halide, was then weighed in red light. Reference to the table of results shows the difference in weight to be inappreciable. The photo-chemical change of silver halide is, perhaps, insignificant in this work because of the large excess of silver present with the silver salt. In any case, the comparative values obtained, indicate the use of ordinary light to be quite safe.

In three electrolyses of sodium chloride conducted especially for the purpose, the liquid in the inner cup, after the current had fallen to 0.05 A., was examined for hypochlorites and chlorates. None was found in any tests. The halogen seemed to be present as halide only. The absence of a significant amount of silver from the electrolyte by solution of the silver anode is consequently proved. For in all the electrolyses only absolutely clear solutions prevailed, and the amount of silver ions in the presence of the excess of chloride must have been extremely small. The maximum solubility of silver chloride in water at 20° is 1.06×10^{-5} moles per liter, hence its solubility product in moles per liter is 1.12×10^{-10}. In determination No. 9, for example, the chlorine found by the nephelometer was 0.00026 gram. Since the volume in which this was contained was 50 cc., the chlorine concentration in moles per liter was 1.5×10^{-4}. The amount of silver ions present in a clear chloride solution of such concentration cannot exceed 1.12×10^{-10} divided by 1.5×10^{-4}, or 0.75×10^{-6} moles per liter or 0.35×10^{-5} grams of silver in 50 cc. (the volume of the liquid in the inner cup).

Moreover, the same lot of mercury was used as cathode in all the determinations. This was distilled until only a small residue remained. The residue was carefully examined for silver. A nephelometric test revealed the presence of 0.0003 gram of the metal. Since this was the total

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quantity of silver transferred in more than fifty analyses of salt, it is quite evident that the effect of transference of silver from anode to cathode in a single electrolysis is negligible.

The matter of occlusion of salt solution in the constantly increasing deposit on the anode was of vital importance and required careful consideration. It seemed quite possible, especially in the concentrated solution that obtained in the beginning of each electrolysis, for the silver halide in its formation to enclose minute quantities of the surrounding liquor; and although the mechanically enclosed water might probably be driven off by drying in the oven, the occluded sodium halide would exert its detrimental effect on the weight of the anode, and consequently vitiate the method for accurate work. The following experiments were therefore carried out. The dried anode after electrolysis was immersed in pure water saturated with distilled ammonia. Solution of the silver chloride resulted, and the anode was thoroughly washed with the ammonia water. Any occluded sodium chloride would be in the ammoniacal solution. On the addition of pure HNO_3 and on boiling, silver chloride was precipitated, but only the chloride ion of the original silver chloride would be affected; any sodium chloride originally occluded would be in the filtrate. (Of course, the usual precautions in filtering silver chloride were observed.) This filtrate was made up to definit volume and its turbidity (extremely slight) determined by the nephelometer. This gave the zero point, so to speak, and to the solution was then added an excess of silver nitrate; a nephelometric reading was taken and the increase in turbidity noted. In three separate instances the maximum opalescence produced did not exceed 0.005 mg., an entirely negligible quantity, indicating quite definitly the absence of occluded chloride. Richards and Wells have conclusively demonstrated that occlusion of mother liquor in precipitates is a function of the concentration of the medium in which the precipitation occurs. Acting on this, in two electrolyses only very dilute solutions obtained; that is, the salt was added in small quantities from time to time, when the fall of the ammeter needle indicated that only minute amounts of salt were undergoing analysis. There was, in these atomic weight values, no significant variation from those resulting on electrolysis of more concentrated solutions, thus again pointing to the absence of salt occlusions.

In three cases the anode, after the usual drying in the oven, was placed in a previously ignited and weighed porcelain evaporating dish, and heated by a protected Bunsen flame until complete fusion of the silver halide resulted. Cooling and reweighing the dish and anode with a suitable counterpoise gave substantially the same values. In two determinations the loss in weight was 0.02 mg., while in the third the balance detected no change in weight. This procedure dispelled the thought of permanent retention of water in the dried deposit, and demonstrated the efficacy

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of the ordinarily employed method of drying the anode. Moreover, the concordance in values obtained by the use of widely different amounts of salt, strengthens the basic thesis that the increase in weight of the anode represents only the halogen content of the salt under analysis.

While waiting for the arrival of the triple gauze anodes a preliminary series of determinations was made with the ordinary double gauze electrode. In all other respects, the apparatus and materials were identical for both series of values. Greater concordance in the final series is to be ascribed to the use of larger quantities of salt as well as to more experience in the manipulation of the method.

The atomic weight of sodium, as given by the International Committee on Atomic Weights for 1910, was taken as 23.00.

In calculating vacuum corrections the following table was used:

	Density at 20°	Correction for 1 gram of substance at 20°, 760 mm.
NaCl	2.14	+0.000418
NaBr	3.1	+0.000244
Ag	10.49	+0.000029
AgCl	5.56	+0.000073
AgBr	6.39	+0.000046
Brass weights	8.4	

Wt. of 1 cc. of air = 0.0012 gram.

By calculating from the approximate amount of halogen present the silver necessary to combine with it, the necessary vacuum correction for silver and silver halide was obtained, since only that weight of the anode actually undergoing change is to be considered in applying the vacuum correction. Thus, the approximate weight of chlorine times 3.04 gives the weight of silver actually attacked, and the correction is made for this and not for the whole anode.

The data for one single determination will be given in detail, to illustrate the mode of procedure. Subsequent record will be made of only the final figures necessary to establish the ratio of sodium to halogen.

WEIGHING OF SODIUM CHLORIDE.

0.070 gram = wts. on pan excess over counterpoise.
+0.00085 gram = rider reading.

0.07085 gram = total weights used.
+0.00003 gram = correction for weights used.

0.07088 gram = apparent excess weight of empty beaker over counterpoise.
1.079 grams = wts. on pan excess over counterpoise.
—0.00062 gram = rider reading.

1.07838 grams = total wts. used.
+0.00001 gram = correction for weights used.
1.07839 grams = apparent excess weight of beaker and NaCl over counterpoise.
—0.07088 gram = apparent excess weight of beaker over counterpoise.

1.00751 grams = apparent weight of NaCl.
+0.00042 gram = vacuum correction.

1.00793 grams = correct weight of NaCl.

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0.61 gram = approximate weight of Cl present in NaCl taken.
0.61 × 3.04 = 1.85 grams = approximate weight of silver combined with chlorine.
0.61 + 1.85 = 2.46 grams = approximate weight of silver chloride formed.
1.85 × —0.00003 = vacuum correction for silver = —0.00006 gram.
2.46 × 0.000073 = vacuum correction for silver chloride = 0.00018 gram.

Weighing of Anode.

3.150 grams = wts. on pan in excess of counterpoise anode.
+0.00024 gram = rider reading.

3.15024 grams = total wts. used.
+0.00010 gram = correction for weights.

3.15034 grams = apparent excess weight of silver anode over counterpoise.
—0.00006 gram = vacuum correction for silver attacked.

3.15028 grams = corrected excess of anode over counterpoise.
3.760 grams = wt. on pan in excess of counterpoise anode.
+0.00097 gram = rider reading.

3.76097 grams = total weights used.
+0.00016 gram = correction for weights.

3.76113 grams = apparent excess weight of silver chloride anode over counterpoise
+0.00018 gram = vacuum correction for silver chloride formed.

3.76131 grams = corrected excess of anode over counterpoise.
—3.15028 grams = corrected excess of anode over counterpoise.

0.61103 gram = correct weight of chlorine found on anode.

Nephelometer Readings.

Standard.	Test.	Ratio.
5.0	1.9	3.80
7.8	3.0	3.84
9.1	3.5	3.84

Correction for chloride in solution = 0.00038 gram chlorine.

Electrical Readings.

	Beginning of electrolysis.							End of electrolysis.
Voltage	3.5	——	3.5	——	3.5	——	3.5	—— 3.5
Amperage ..	0.91	——	0.52	——	0.22	——	0.12	—— 0.038
Time	9.8	——	9.20	——	9.45	——	10.15	—— 10.46

(hence 1 hour, 38 minutes)

0.61103 gram Cl found on anode.
+0.00038 gram Cl determined in nephelometer.

0.61141 gram total chlorine found.
1.00793 grams NaCl taken.

1.00793 : 0.61141 = 23.00 + X : X. X = atomic weight of chlorine.
X = (23.00) (0.61141)/1.00793 — 0.61141
X = 35.465.

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Determinations 10, 12 and 24 were carried out in darkness as mentioned above. After drying and weighing as usual, the halides on anodes in determinations 9, 11 and 20 were fused as previously described. No significant change of weight was observed. In determinations 17, 18, 19 and 27, the pure silver disc anode was used.

PRELIMINARY SERIES.

Sodium Chloride.

Number of determination.	NaCl taken in grams.	Cl found on anode.	Cl determined in nephelometer.	Cl total.	Atomic wt. of chlorine. Na = 23.00.
1....	0.81495	0.49423	0.00009	0.49432	35.460
2....	0.79370	0.48128	0.00007	0.48135	35.445
3....	0.88940	0.53952	0.00010	0.53962	35.483
4....	0.45642	0.27666	0.00013	0.27679	35.441
5....	0.43884	0.26612	0.00006	0.26618	35.458
6....	0.44239	0.26818	0.00010	0.26828	35.440
7....	0.64942	0.39381	0.00006	0.39387	35.449
8....	0.53706	0.32535	0.00046	0.32581	35.473
				Average =	35.456 ± 0.0037

FINAL SERIES.

Sodium Chloride.

Number of determination.	NaCl taken in grams.	Cl found on anode.	Cl determined in nephelometer.	Cl total.	Atomic wt. of chlorine. Na = 23.00.	Atomic wt. of sodium. Cl = 35.458.[1]
9....	1.02234	0.61988	0.00026	0.62014	35.463	22.997
10....	1.02221	0.61957	0.00049	0.62006	35.463	22.997
11....	2.43474	1.47654	0.00038	1.47692	35.466	22.996
12....	1.46370	0.88780	0.00009	0.88789	35.466	22.995
13....	0.56934	0.34522	0.00012	0.34534	35.460	22.999
14....	1.00793	0.61103	0.00038	0.61141	35.465	22.995
15....	1.06501	0.64579	0.00021	0.64600	35.459	22.999
16....	2.16720	1.31442	0.00018	1.31460	35.463	22.997
17....	2.75219	1.66904	0.00035	1.66939	35.460	22.999
18....	0.92900	0.56337	0.00012	0.56349	35.458	23.000
19....	1.83527	1.11294	0.00030	1.11324	35.462	22.998
				Average =	35.462 ± 0.0005	22.997 ± 0.0003

Sodium Bromide.

Number of determination.	NaBr taken in grams.	Br found on anode	Br determined in nephelometer.	Br total.	Atomic wt. of bromine. Na = 23.00.	Atomic wt. of sodium. Br = 79.920.[1]
20....	1.05343	0.81775	0.00028	0.81803	79.927	22.998
21....	1.33360	1.03542	0.00019	1.03561	79.932	22.997
22....	1.95652	1.51875	0.00061	1.51936	79.936	22.995
23....	5.02976	3.90513	0.00073	3.90586	79.930	22.997
24....	2.09332	1.62545	0.00009	1.62554	79.925	22.998
25....	6.46697	5.02162	0.00016	5.02178	79.920	23.000
26....	5.54733	4.30740	0.00028	4.30768	79.923	22.999
27....	7.03901	5.46575	0.00031	5.46606	79.926	22.99
				Average =	79.927 ± 0.0014	22.998 ± 0.0003

[1] F. W. Clarke, *Loc. cit.*

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Since the above article was published in separate form as a thesis, Dr. W. A. Noyes has called attention to the fact that the work is really a determination of the ratios between sodium and chlorine and sodium and bromine. The accepted value for the atomic weight of sodium, 23.00, is based on oxygen through either silver or chlorine or bromine and hence, as a piece of atomic weight work, the value of sodium is to be calculated. This was accordingly done and with the results given in the last column of the table. The value of chlorine was taken as 35.458, of bromine 79.920.[1]

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THE FRACTIONATION OF THE YTTRIUM EARTHS BY MEANS OF THE SUCCINATES.

BY R. C. BENNER.

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During the past decade material contributions have been made to the study of the yttrium group of the rare earths. Among these it has been shown by Lenher that, through the agency of the succinates, considerable rapidity can be arrived at in the process of separating various mixtures of these earths. The succinates of the yttrium group are finely divided crystalline precipitates, which are best formed by the addition of a solution of neutral ammonium or sodium succinate to a neutral nitrate solution of the yttrium earths. This precipitate is of especial interest because the time of formation is so greatly delayed that it is possible for equilibrium to become more readily established. Under these conditions the separation is more sharply performed than if precipitation took place instantaneously.

In order to test the applicability of the succinates as reagents in the yttrium group, the yttrium earths were extracted from a number of rare earth minerals of widely differing character and the separation studied in some detail.

Samarskite.—The yttrium earths were extracted from samarskite and studied in considerable more detail than previously reported.[2] The atomic weight determinations and the study of the absorption spectra were used as a continual control on the process of fractionation. The atomic weight determinations were carried out with sufficient accuracy by means of the oxalate method. The absorption spectra studies were made by means of a Steinheil grating spectroscope, similar to the one described by Dennis.[3] The earths having the highest atomic weights were precipitated first, showing that the succinates of the earths having

[1] F. W. Clarke, *Loc. cit.*

[2] THIS JOURNAL, 30, 575.

[3] *Ibid.*, 24, 415.

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lower atomic weights were the more soluble. In all cases the color of the oxides and the strength of the absorption spectra varied in the same ratio as did the atomic weights, all of which demonstrated that erbium and the other heavy earths concentrated in the first fractions, while yttrium concentrated in the last. Typical illustrations of this separation were given in the following series of atomic weights. A, 130, 116, 104; B, 123, 115, 98.5; C, 114, 108, 99.7; D, 104, 97.

Monazite.—In order that the influence of various factors in the succinate method might be verified by experiment, several hundred grams of the yttrium earths were separated from monazite, the solution being effected in nitric acid in such a manner that the solution formed was neutral to methyl orange.

A sodium succinate solution was made by adding sodium hydroxide to succinic acid until the solution was neutral to phenolphthalein, after which the strength was determined. An ammonium succinate solution of equal strength was prepared by the addition of ammonia to succinic acid until neutral to litmus. Sixty cc. of the yttrium earth nitrate solution, containing 7.84 grams of rare earth oxides, were diluted to one liter and fractioned in various ways, so that six fractions were obtained in each case.

Experiment 1.—The effect of fractionation in dilute was compared with the same operation in a strong solution, the strength of the succinate being varied as well as that of the earths.

Experiment 2.—The relative value of sodium succinate as a precipitating agent was compared with that of ammonium succinate.

Experiment 3.—The rapid addition of the succinates was compared with the addition of the same reagent drop by drop.

Experiment 4.—The effect of stirring during precipitation was studied.

Experiment 5.—The addition of various substances to the solution, such as sodium or ammonium acetate and nitrate, was studied.

The separation was most satisfactorily made when the precipitating reagent was added drop by drop. Sodium succinate appeared to be slightly superior to ammonium succinate as a precipitating reagent. The separation was apparently not aided by the presence of sodium acetate or nitrate, or by the corresponding ammonium salts.

Behavior of Sodium Succinate towards Mixtures of the Cerium and Yttrium Groups.—The material chosen for this experiment was a mixture of the monazite earths containing a large portion of the earths of the cerium group. The oxalates of this mixture were ignited to the oxide, dissolved in nitric acid, and evaporated to a sirup. The cerium was reduced to the cerous form by hydrogen peroxide and the excess destroyed by boiling the solution. The solution containing sixty-one grams of these oxides, in form of the neutral nitrates, was diluted to one liter and frac-

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tionally precipitated by means of a ten per cent. sodium succinate solution, 100 cc. of the solution being added at one time. The fractions, after being ignited to the oxide, were of a similar dark brown color, except the last two, which were of a lighter shade. Their atomic weights were as follows: 149.5, 147.0, 147, 150.0, 149.0, 146.0, 143.0, 143.0, 143.0. It was evident that there was very little separation of the elements of lower atomic weight from those of higher. The absorption spectra of these fractions failed to show any difference except in case of the last, in which the didymium lines were fainter and the oxide had a slightly paler color than that of the previous fractions.

Xenotime.—Ninety-five grams of the finely powdered mineral were thrown, in small amounts at a time, into fused hydrogen ammonium sulfate. The greenish mass was extracted with water containing a little hydrochloric acid, and the extraction continued until ammonia no longer gave a precipitate. This was then treated with an excess of potassium sulfate and the soluble double sulfates precipitated with oxalic acid and converted to the oxides by ignition. These oxides were converted to the neutral nitrates and a solution of 6.83 grams per liter was fractioned with a 2 per cent. sodium succinate solution. In th s instance the sodium succinate solution was added drop by drop, the solution being kept at a boiling temperature and constantly stirred with a mechanical stirrer. Each fraction was filtered after the addition of 12.5 cc. of the sodium succinate solution, and the treatment repeated on the filtrate, the volume being kept at one liter during the experiment. The following different fractions were obtained: 112.5, 109.4, 105.7, 101.6, 98.5. By comparison of the different fractions as to color of the ignited oxides and the absorption spectra, it was noted that elements of higher atomic weight concentrated in the first fractions, while yttrium accumulated in the mother liquor. This followed in all respects the yttrium earths from samarskite.

Gadolinite, from Langesundfiord, Norway.—Ninety-five grams of the finely powdered mineral were treated with aqua regia until the residue was colorless, the solution evaporated to dehydrate the silica, the residue extracted with water, and to the clear solution ammonium oxalate added as long as a precipitate formed. These oxalates were converted to the oxides, dissolved in the least possible amount of hydrochloric acid, treated with an excess of potassium sulfate in the cold and the soluble double sulfates precipitated by means of oxalic acid. Twenty-five grams of the oxides were converted to the neutral nitrates, diluted to one liter and fractioned by successive additions of 40 cc. of a 14 per cent. solution of sodium succinate. The atomic weights of the fractions obtained were: 113.8, 109.9, 108.0, 107.3, 105.6, 103.2, 98.1, 95.1.

The yttrium earths from this specimen of gadolinite were in all respects similar to those from xenotime, as far as the behavior toward

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sodium succinate was concerned. The color of the oxides and the absorption spectra were found to be similar to the earths from xenotime, except for the more gradual change in atomic weights, which latter would be expected on account of the greater number of fractions.

Fergusonite, from Gaalenerne, Norway.—One hundred and five grams of the finely powdered mineral were fused with 400 grams of potassium acid sulfate. The fused mass was pulverized, extracted with ice water, and washed with cold water until the washings failed to give a precip tate with ammonia. The solution was treated with ammonia and the precipitate obtained dissolved in nitric acid and heated for several days, water being added to replace that lost by evaporation. The precipitated metallic oxides were filtered off, the filtrate neutralized, and the earths precipitated by means of oxalic acid. To the hydrochloric acid solution of the earths potassium sulfate was added and the soluble double sulfates, when free from didymiums, were precipitated with oxalic acid and converted to the oxides. Ten and eighty-five hundredths grams of the oxides were changed to the nitrates, the solution made neutral to methyl orange, and diluted to one liter. This solution was fractioned by the addition of 25 cc. portions of a 5 per cent. sodium succinate solution, the solution being constantly stirred and the volume kept constant. Atomic weight and spectroscopic observations were made on the various fractions. The atomic weights were: 115.4, 112.4, 110.5, 102.5.

This series was of more interest than any of the preceding, as the spectroscopic observations showed the mixture to be of a more complex character. The separation, however, appeared to be somewhat sharper in the more rapid disappearance of the number of lines. The oxides were found more varied in color than was the case with the other minerals.

Euxenite, from Arendal, Norway.—Three hundred grams of the mineral were treated in a lead dish with hydrofluoric acid until the action ceased. The insoluble fluorides were washed with hydrofluoric acid until most of the soluble matter was extracted and converted to the sulfates by heating with concentrated sulfuric acid, the excess of which was driven off. After th s treatment the pulver zed sulfates were dissolved in ice water. The solution was treated with potassium sulfate, the soluble double sulfates precipitated with oxalic acid, converted to the oxides and then to the nitrates. The yttrium earths were then fractioned with sodium succinate, and in all respects appeared to be quite similar to those obtained from fergusonite. The atomic weights of the fractions were: 115.5, 112.7, 110.0, 108.2, 104.5, 102.5.

Gadolinite, from Texas.—Three hundred grams were treated with hydrofluoric acid, the insoluble fluorides converted to sulfates, the cerium didymium group removed by potassium sulfate, as usual. Twenty-seven grams of the oxides obtained were converted to the neutral nitrates

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and dissolved in one liter of water. This solution was fractionally precipitated with a 5 per cent. solution of sodium succinate. The atomic weights of the various fractions were: 122.0, 117.0, 112.0, 112.0, 108.5, 103.0, 102.5. The absorption spectra showed that the earths varied in the same manner as did the atomic weights.

Keilhauite, from Tvedestrand, Norway.—Fifteen hundred grams of the mineral were treated with hydrofluoric acid. The insoluble fluorides were converted to the sulfates, and the sulfate solution submitted to treatment with potassium sulfate in order to remove the cerium-didymium group. Seventeen grams of the oxides thus obtained were converted to the neutral nitrates and diluted to one liter. This solution was fractioned with a 5 per cent. solution of sodium succinate. The fractions showed atomic weights of 116.5, 116.5, 108.0, 104.0, 104.0. In general, the atomic weights were somewhat higher than the earths from fergusonite, but in all other respects were found to be identical..

Deportment of the Succinates of the Erbium Earths.—The study of these minerals indicated that sodium succinate showed the same general behavior towards different mixtures of the earths having low atomic weight. The separation seemed to be more marked as the average atomic weight of the mixture increased. In order to experimentally investigate this in more detail, erbium earths were extracted from monazite and samarskite. The erbium earths from monazite were separated from other members of the yttrium group by the chromate method. From a neutral nitrate solution containing 10 grams of these oxides per liter, fractions were obtained by means of a 5 per cent. sodium succinate solution. The atomic weights were: 152.5, 154, 148.5, 139, 124. A fraction of the samarskite earths, showing an atomic weight of 122.5 obtained by the succinate method, was converted to the neutral nitrates and again fractioned by the sodium succinate method. The atomic weights of these fractions were as follows: 133.0, 134.0, 131, 127.0, 122.5, 112.5, 103.0, while the color of the oxides varied from nearly white to brown. It was apparent, therefore, that the succinate method gave a more rapid separation with earths having comparatively high atomic weight.

Composition of Yttrium Succinate.—A few succinates have been made and analyzed. Czudnowicz and Cleve[1] (analysis given) report the succinate of lanthanum as $La_2(C_4H_4O_4)_3.5H_2O$. Cleve reports the succinate of samarium[2] (without analysis) as $Sm_2(C_4H_4O_4)_3.5H_2O$, also the succinate of yttrium[3] (with analysis) as $Yt_2(C_4H_4O_4)_3.4H_2O$, (with analysis) the succinate of erbium as $Er_2(C_4H_4O_4)_3,9H_2O$.[4] Czudnowicz[5] tells how to

[1] *Bull. soc. chim.*, 21, 202.
[2] *Ibid.*, 43, 172.
[3] *Ibid.*, 18, 296.
[4] *Ibid.*, 43, 172.
[5] *Jahresb.*, 1861, 189

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make the succinate of cerium and gives some of its properties. It is reported as $Ce(C_4H_4O_4).1.5H_2O$. Recently Sir Wm. Crookes made the succinate of scandium, to which he gave the formula $Sc_2(C_4H_4O_4)OH.H_2O$.

Yttrium was prepared in a fairly pure condition from mixed residues by the chromate method. The material selected gave only the slightest trace of absorption spectra when observed in a saturated solution 20 cm. thick. A neutral solution of this yttrium as nitrate was precipitated in a dilute solution at a boiling temperature by the addition of sodium succinate, drop by drop, with constant stirring. The precipitate was filtered, washed with boiling water and dried over sulfuric acid until the weight was constant. The crystallin compound prepared in this manner was pure white. Analysis showed it to be a normal succinate.

THEORETICAL FOR $Yt_2(C_4H_4O_4)_3.2\frac{1}{2}H_2O$ Yt = 90.1.

	Theoretical.	Found.	
Yt	31.40	31.89	31.79
C	25.12	25.83	25.45
H	3.00	3.28	3.30

Solubility of Yttrium Succinate.—The salt was introduced into a flask with distilled water, connected with a reflex condenser, boiled for seven hours and filtered hot. One liter, when evaporated to dryness in a platinum dish, gave 0.054 gram of oxide, equivalent to 0.135 gram of yttrium succinate. The same experiment was repeated, the boiling being continued in this instance for twenty-one hours, and showed a solubility of 0.152 gram of the succinate. These determinations showed that the normal succinate was only sparingly soluble in water. Qualitative observations seemed to indicate that the solubility was greatly affected by the presence of an excess of either yttrium nitrate or sodium succinate.

Conclusion.

As a precipitation method the use of the succinates can be highly recommended. The precipitates are readily handled, and by ignition converted to the oxides. Should it be desirable to conduct this separation on a scale in which the question of economy is to be considered, the succinates can easily be converted to the hydroxides by means of sodium hydroxide.

The best separation can be performed by precipitating a nearly neutral boiling solution of the nitrates with sodium succinate, added drop by drop. It makes very little difference whether the solution is stirred or not. As long as the concentration of the yttrium earths does not exceed 2 to 3 per cent. the separation is satisfactory.

Yttrium succinate is a normal salt having the formula $Yt_2(C_4H_4O_4)_3.2.5H_2O$. This is a white salt, slightly hygroscopic and very nearly insoluble in water, 0.0574 gram of the oxide, equivalent to 0.1435 gram of the succinate, being soluble in one liter of boiling water.

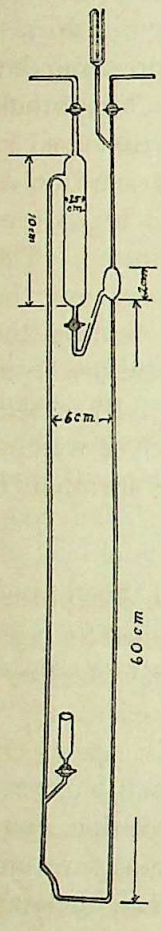
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The author wishes at this time to express his thanks to Professor Victor Lenher for valuable suggestions in this work, and to H. S. Miner, of the Welsbach Light Company, for a large part of the material.

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NOTE.



A Modified Boltwood Pump.—The modification of the Boltwood pump, which is represented by the accompanying diagram, may be of interest to those engaged in work which requires a high vacuum.

The original pump as stipulated by Boltwood[1] consists of a large bulb, 6 cm. diameter, which acts as the reservoir for the mercury and a smaller bulb of two to three centimeters diameter. The whole apparatus is about 120 cm. long, and 30 cm. wide, using from 700 to 1000 grams of mercury. The apparatus shown in the diagram is at present in use in this laboratory, and gives just as efficient service as the larger forms—sparks being obtained in Pflücker tubes after three minutes' operation, and within a quarter of an hour the pressure cannot be measured on an ordinary manometer—occupies only one-third the space, and requires 100 g. Hg for successful operation.

It might be added in this connection, that there is considerable deviation from the prescribed internal diameter of the dropping tube (2.5 mm.) in the manufactured forms; and it has been observed by the author, that a slightly larger tube refuses to give low vacuums—obviously while a tube smaller than 2 mm. works so slowly as to be comparable to the older hand-lift varieties.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

SOME DERIVATIVES OF PARA-AMINOBENZOHYDROL.[2]

BY HENRY A. TORREY AND C. W. PORTER.

Received November 11, 1910.

This paper is a report of the beginning of the work in an extensive research on derivatives of para-aminobenzophenone which is being con-

[1] *Am. Chem. J.*, 19, 76 (1897).

[2] This research was suggested by the late Professor Henry A. Torrey and most of the experimental work was done under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.

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tinued in this laboratory. Para-aminobenzophenone was prepared in large quantities from aniline and benzoyl chloride according to the method of Döbner[1] and the ketone was reduced to the corresponding secondary alcohol called by Kippenberg "*p*-amidobenzhydrol".[2] The alcohol crystallizes from hot water in long, slender, colorless needles melting at 121°. A number of new derivatives of this compound were prepared as follows:

Azo Dyes.

Benzohydrol-4-azo-β-naphthol.—A beautiful red dye was prepared by diazotizing para-aminobenzohydrol and coupling it with β-naphthol. To accomplish this four grams of the secondary alcohol were dissolved in cold,[3] dilute hydrochloric acid and diazotized at zero with a solution of potassium nitrite. A solution of three grams of β-naphthol in sodium hydroxide was then added and a bright red dye was precipitated. The precipitate was washed with caustic soda solution to dissolve out the excess of β-naphthol, then with dilute hydrochloric acid to remove the last trace of free para-aminobenzohydrol. The residue was then dissolved in acetone and reprecipitated by adding a little water or dissolved in benzene and precipitated by the addition of gasoline. The product was insoluble in acids or bases and melted at 169.5°. The formula is $C_6H_5CHOH—C_6H_4—N:N—C_{10}H_6OH$.

Found: N, 8.00. Calculated, 7.91.

Para-aminobenzophenone when diazotized and treated with β-naphthol yielded a dye of a much lighter red color. It was easily purified by crystallization from hot alcohol. It separated on cooling as a light feathery substance resembling cotton wool, except in color. It melted at 185°–186.5°. The sample analyzed contained 8.17 per cent. N. The calculated value for $C_6H_5—CO—C_6H_4N_2C_{10}H_6OH$ is 7.96.

Benzohydrol-4-azodimethylaniline. — Para-aminobenzohydrol diazotized and coupled with dimethylaniline yielded a fine dye crystallizing from hot alcohol in red sparkling flakes, melting sharply at 145°. The compound was readily soluble in glacial acetic and hydrochloric acids, acetone, chloroform, ether or benzene. It was precipitated from the latter by gasoline and crystallized from a hot alcoholic solution on cooling. Its formula is $C_6H_5—CHOH—C_6H_4—N:N—C_6H_4N(CH_2)_2(p)$.

Found: N, 12.90. Calculated, 12.70.

Since para-aminobenzohydrol readily yields an anhydride with cold concentrated hydrochloric acid or when warmed with dilute hydrochloric acid, it was thought advisable to determin whether or not the hydroxyl

[1] *Ann.*, 210, 260.

[2] *Ber.*, 30, 1136.

[3] When hot hydrochloric acid is used the anhydride of aminobenzohydrol, $C_6H_5—CHC_6H_5—NH$, is precipitated.

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group remained unaltered in the molecule when subjected to the action of the cold dilute hydrochloric acid in which it was always diazotized. The dimethylaniline derivative furnished a good compound to work with in settling this question for in it there is no possibility of the existence of a hydroxyl group except the one originally present in the secondary alcohol.

From this dye an acetyl derivative was prepared by treatment with sodium acetate and acetic anhydride, the nitrogen content of which was 11.31 per cent. This is in close agreement with the theoretical value 11.27 per cent. and proves the presence of the hydroxyl group. The compound responded also to the Schotten-Baumann test (benzoyl chloride and sodium hydroxide), giving a well crystallized benzoyl derivative.

Condensed molecules of the diazo compounds would give practically the same analyses for nitrogen as would single molecules. The presence of the hydroxyl group in the dimethylaniline dye made it fairly certain that there had been no condensation, for condensation could hardly be expected to take place except by the elimination of one molecule of water from two molecules of the dye, leaving a compound with an ether formula and containing no hydroxyl group. The question was more definitly settled, however, by a determination of the molecular weight. The boiling-point method was used and benzene employed as a solvent. The average of four determinations for the dimethylaniline derivative of para-aminobenzohydrol was 345. The calculated value for the formula given above is 331.

Aldehyde Condensations.

Salicylal-para-aminobenzohydrol. — Equimolecular quantities of para-aminobenzohydrol and salicylaldehyde were dissolved in alcohol and heated on a steam bath for two hours. Upon cooling and diluting with a little water a yellow precipitate was produced. This condensation product was readily soluble in benzene, chloroform, acetone, alcohol or ether, and practically insoluble in water. It was, however, rapidly hydrolyzed by water, even at ordinary temperatures, and on that account was purified with difficulty. The addition of a little water was necessary to throw the compound out of solution and unless the temperature of the alcohol solution was reduced to zero or below before water was added, a distinct odor of salicylaldehyde was produced. At the temperature of boiling water the compound was quickly and completely hydrolyzed.

The sample analyzed was recrystallized several times from alcohol at zero and melted at 76°–79°. The formula is C_6H_5—CHOH—C_6H_4—N: CH—C_6H_4OH(*o*).

Found: N, 4.70. Calculated, 4.62.

Para-aminobenzophenone formed a similar condensation product with salicylaldehyde, but unlike the hydrol derivative, it crystallized

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from alcohol on cooling and was therefore more easily purified. It was a yellow solid soluble in benzene, acetone, or chloroform, insoluble in sodium hydroxide and sparingly soluble in cold alcohol. Formula, $C_6H_5—CO—C_6H_4N:CH—C_6H_4OH$.

Found: N, 4.84. Calculated, 4.65.

β-Naphthol-α-methylol-para-aminobenzohydrol.—Equivalent quantities of para-aminobenzohydrol and β-naphthol aldehyde were dissolved in a small quantity of 95 per cent. alcohol and boiled for one hour. On cooling, a yellow crystallin substance separated out which was readily soluble in alcohol, acetone, alkalis, or hot benzene, but crystallized from the latter on cooling in a fair state of purity. Its melting point was ound to be 167.5°. Formula, $C_6H_5—CHOH—C_6H_4N:CH—C_{10}H_6OH$.

Found: N, 3.98. Calculated, 3.98.

The corresponding ketone, prepared in a similar way with para-aminobenzophenone, was a fine yellow crystallin substance melting at 152°. It was insoluble in alkalies, in this respect differing from the hydrol derivative.

It was easily purified by crystallizing from hot methyl alcohol. Formula, $C_6H_5CO—C_6H_4N = CH—C_{10}H_6OH$.

Found: N, 3.90. Calculated, 3.99.

The insolubility of this last compound in alkalies would be expected as it fulfils both the conditions found necessary[1] to produce this phenomenon in other cases—the free hydroxyl group is ortho to a large side chain, and another substituting group is present on the benzene ring to which the hydroxyl is attached—in this case the C_4H_4 of naphthalene which has been found to be specially effective; but the addition compound of salicylaldehyde and para-aminobenzophenone does not conform to the second of these conditions and its insolubility in alkalies is therefore not in harmony with the general rule. Only two or three other exceptions to the above rule have been found. This substance therefore will be studied further in this laboratory.

[Contribution from the Research Laboratory, Roosevelt Hospital, New York.]

PHENOLPHTHALEIN AND ITS COLORLESS SALTS.

(Potassium Salt of Phenolphthalic Acid.)

By P. A. Kober and J. Theodore Marshall.

Received November 17, 1910.

Contents.—(1) Introduction. (2) The Study of Speed of Reaction: (*a*) Colorimetrically; (*b*) Electrolytically. (3) The Study of Concentrations at Equilib-

[1] Torrey and Kipper, This Journal, 30, 841 (1908).

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rium. (4) The Isolation and Analysis of the Colorless Salt (Tripotassium Phenolphthalate). (5) Discussion of Results. (6) Summary. (7) Addendum.

(1) Introduction.

While studying different chemical tests for blood, we found that certain substances inhibited[1] the reactions. A futher investigation of this phenomenon, using phenolphthalein as suggested by Kastle,[2] showed that the color of a standard solution of phenolphthalein faded, even after the possible action of carbon dioxide had been excluded. This fact, noted by McCoy,[3] Acree,[4] Kastle, and others, had not been thoroughly investigated from a quantitative point of view, so it was with the object of determining the exact reaction and extent of the fading under various conditions, that these experiments were undertaken.

Believing that the colorless salts existed in the presence of free alkali only, and consequently could not be isolated, we attempted to solve the problem by studying the rate of reaction, and the concentrations at equilibrium. When our experiments were almost completed, we read the excellent review of the phenolphthalein question, given by Curtiss,[5] in his article on the theory of color in organic compounds. Finding our results to be in harmony with the ideas expressed in his article, we intended publishing our work, both as a confirmation of previous results, and also to show the effect of fading on blood tests.

Attempts had been made, both here and abroad, to isolate the heretofore hypothetical colorless salt, but without success. Since we have been able to obtain a precipitate of the salt, in an alkaline solution and have developed a method of purification which yields an abundance of beautiful colorless crystals of this salt, we believe the publication of all our experiments is perfectly justifiable, although our results are in part repetitions of previous experimentation. It may be mentioned, had we known the field to have received so much attention and disputation, we should not have entered it, but considering it our duty to do so now, we do not hesitate to submit the following results.

(2) The Study of Speed of Reaction.

In order to study the rate of fading with the Duboscq colorimeter we found it necessary to establish a permanent standard for comparison

[1] Kober, Lyle, and Marshall, *J. Biol. Chem.*, July, 1910. Since the publication of this note on the inhibitive action of tannic and gallic acids, on blood tests, we found that nearly all the polyhydric phenols and polyhydroxymonocarboxylic phenols, as pyrocatechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol; protocatechuic, 2,4-dioxybenzoic, gentisinic, gallic and tannic acids; and other substances, like indole and skatole, as well as uric acid, inhibit the reactions. The phenomenon is being studied in this laboratory with the view of eventually obtaining a satisfactory blood reagent.

[2] Kastle, Pub. Health and Marine Hosp. Service, *Bull.* 59.

[3] McCoy, *Am. Chem. J.*, 31, 503 (1904).

[4] Acree, *Ibid.*, 42, 122.

[5] Curtiss, THIS JOURNAL, 32, 795.

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as the color of the standard phenolphthalein solution varied with the slightest change of alkalinity. A set of Lovibond tints[1] fulfilled this requirement.

Our first experiment was to follow the change in a determinable amount of color, after an excess of alkali had been added. For this purpose 2.000×10^{-6} gram-molecules (0.00064 g.) phenolphthalein was dissolved in 100 cc. of water after 1.093×10^{-2} gram-molecules of alkali had been added. At various intervals the amount of color was determined, and plotted against time. The points obtained indicated that the fading followed a regular curve resembling that of an irreversible monomolecular reaction. The constants of the equation, however, as shown below, were not good. The color never faded entirely, but seemed to come to an equilibrium. When the values were substituted in a formula for an opposing unimolecular reaction, $1/t \log E/E-X = K_1 + K_2$, a fairly good constant was obtained, although no effort was made to keep the temperature constant.

TABLE I.

Time.	X.	Irreversible. K.	Balanced reaction. $K_1 + K_2$.
0	0	....	....
1	4.5	0.0341	0.0334
3	19.0	0.0340	0.0370
6	34.0	0.0330	0.0358
10	50.0	0.0328	0.0366
15	66.5	0.0316	0.0362
20	76.4	0.0314	0.0371
30	86.5	0.0290	0.0380
40	90.0	0.0260	0.0366
45	91.0	0.0232	0.0365

At equilibrium $X = 93.2$ $1-X = 6.8$ $K_1/K_2 = 93.2/6.8$

According to this formula the constant of the direct reaction is 0.0341, and that of the reverse reaction 0.00238. (The above values hold for this amount of alkali and dilution only.)

That alkali actually takes part in the fading as a chemical reaction was demonstrated by studying the change in conductivity. A slight change of alkali cannot be very accurately determined as the conductivity of the alkaline solution is very high. Notwithstanding this, by carefully regulating the temperature of the solution, a curve of conductivity values was obtained which approximated that of a dimolecular reversible reaction.

After isolating the tribasic salt, we attempted to study the reverse action alone, by neutralizing the alkali as rapidly as formed, but here encountered a new difficulty: *i. e.*, on the addition of a weak acid (acetic) to an aqueous solution of the tribasic salt, the acid was neutralized with extreme rapidity until two gram-molecules of acid had been added. After

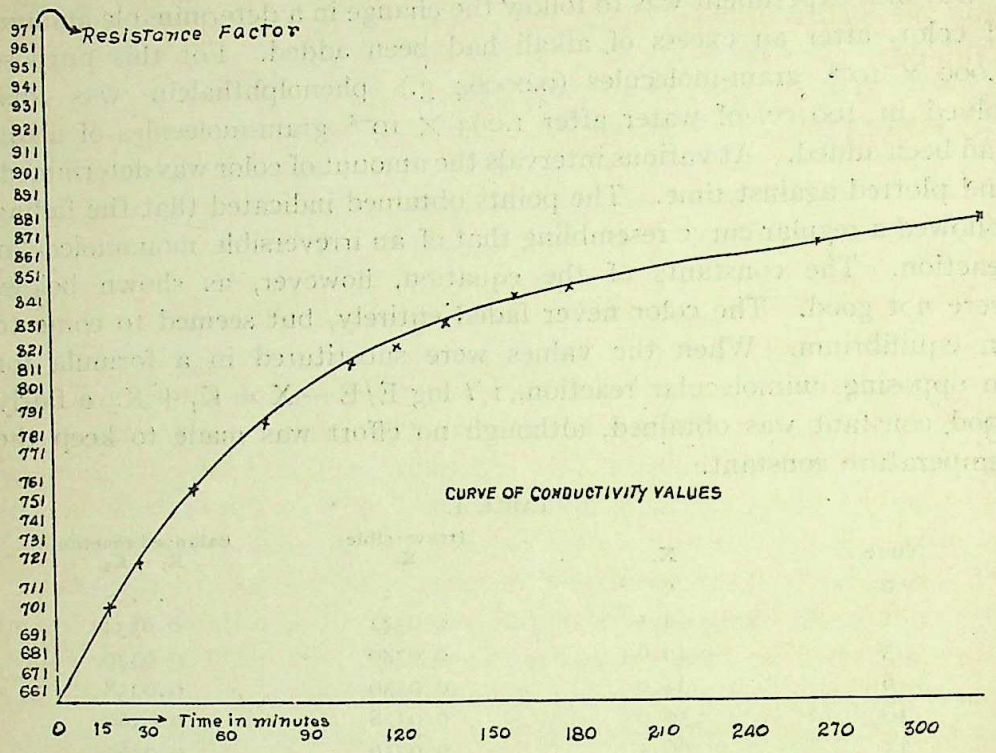
[1] Eimer & Amend, *Lovibond Tints*, 50 (1180 and Z 3.1 (200)).

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this point an apparently new reaction began, and the monobasic colorless salt of phenolphthalic acid decomposed very slowly.

As the number of molecules that enter into a reaction can be more definitly determined from conditions at equilibrium than from the study



of the speed of reaction, a series of equilibrium experiments was made in which the concentrations of the constituents were varied.

(3) The Study of Concentrations at Equilibrium.

0.001258 g. phenolphthalein was dissolved in varying amounts of 0.450 *N* KOH and made up to 100 cc. At room temperature we found:

TABLE II.

Color, per cent. (*a*).	Cc. KOH (*b*).	Colorless, per cent. (*c*).	Constant = $a \times b/c$.
41.7	3	58.3	21.8
37.1	4	62.9	23.6
30.6	5	69.4	22.1
25.1	7	74.9	23.5
19.6	10	80.4	24.4
13.2	15	86.8	22.8
8.85	20	91.1	19.6
7.06	25	92.9	19.0
4.70	35	95.3	17.3

The slight decrease of the constant in the first part of the series may be attributed to the absorption of carbon dioxide during the measurements, and to hydrolysis of the dibasic salt. The lowering of the constant

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at the end of the series is as yet unexplained. Two hypotheses may be brought forward, but definit proof of their correctness is lacking (see Discussion).

When the water concentrations were changed, the amount of alkali and of phenolphthalein being kept constant, the following values were obtained:

TABLE III.

Water conc. (d).	$a \times b/c \times d = K$.	Water conc. (d).	$a \times b/c \times d = K$.
1	6.35	1	6.37
2	6.65	2	6.24
1	6.45	4	5.18
2	5.87		

The great difficulty encountered here was the measurement of faintly colored solutions.

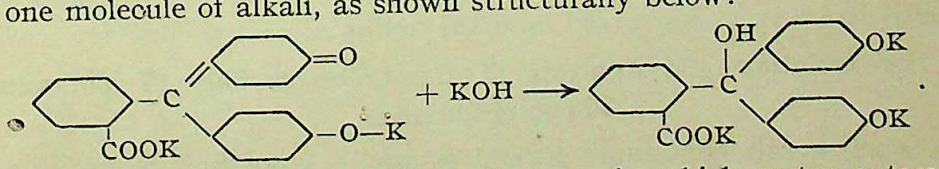
Assuming that it is not a dissociation phenomenon, these equilibrium studies prove that water takes part in the reaction, and consequently water should be included in the equation. Our experiments show unmistakably that one molecule of colored salt combines with another molecule of alkali to form a colorless compound; and that one molecule of water enters into the reverse reaction. As the colored salt, isolated by Meyer and Spengler, was found by them to be dibasic, the colorless salt must then be, as suggested by Green and Perkin, the tribasic salt of phenolphthalic acid. We also prepared the red salt in two different ways and found it to be essentially dibasic.

A definit amount of standard alkali was treated with a weighed portion of phenolphthalein. After standing, the undissolved portion was filtered, dried and weighed. From these weights the following data were obtained:

Phenolphthalein.	Alkali.	Residue.	Theoretical (for dibasic).
1.0057 g.	13.80 cc. $N/10$	0.784 g.	0.786 g.
2.0005	34.50 cc. $N/10$	1.444	1.450
1.380	43.40 cc. $N/10$	0.675	0.695

The discrepancy between the theoretical and the actual amounts is due no doubt to hydrolysis and to the solubility of free phenolphthalein in the water used for washing the residues.

From the above data it may be readily seen that the tribasic salt of phenolphthalic acid is formed from the red compound by the addition of one molecule of alkali, as shown structurally below:

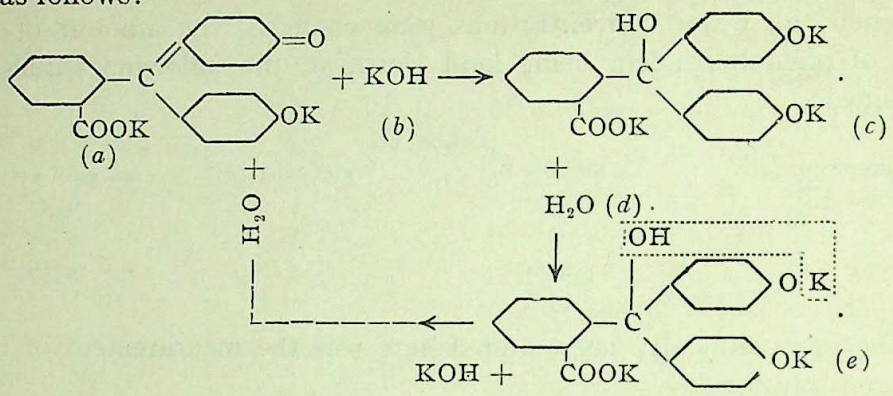


This equation does not indicate the way in which water enters the reverse reaction. As will be discussed in the summary, this phenomenon

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may be due to dissociation, and therefore may not require a chemical explanation. The balanced reaction, written to include water, appears to us as follows:



In order that this equation may fit the formulas and data given elsewhere in this paper, compound "*e*" is assumed to split up into "*a*" very rapidly. This assumption is warranted by the fact that phenolphthalic acid cannot be readily isolated by neutralizing its potassium salt in aqueous solution, even at —10°.

The following studies corroborate our series No. 3. Varying amounts of phenolphthalein were dissolved in 4.50 *N*/10 KOH and made up to 100 cc. At room temperature the following values were found:

Phenolphthalein.	Colored salt (*a*).	Cc. KOH (*b*).	Colorless salt (*c*).	Water (*d*).	K = *a.b*/*c.d*.
0.229 g.	25.4 per cent.	24.50	74.6 per cent.	100	83
0.307	32.1 per cent.	18.00	67.9 per cent.	100	84
0.395	43.0 per cent.	11.95	57.0 per cent.	100	90
		.....			
0.229	0.0060 gram	18.00	0.2230 gram	10	48
0.229	0.0148 gram	18.25	0.2142 gram	25	50
0.229	0.0530 gram	19.55	0.1760 gram	100	54
0.229	0.0289 gram	18.75	0.2000 gram	50	59
0.229	0.0907 gram	20.85	0.1383 gram	250	55

In these experiments the amount of alkali was calculated as the amount which remained after allowing for that portion in combination with dibasic and tribasic phenolphthalein. The temperature was subject to the usual variations of room temperature.

The equation above, which may also be written in the ionic form, permits the use at equilibrium of $a.b/c.d = K$ when the reverse reactions are assumed to be very slow or nil, and the action almost exclusively cyclic.

(4) The Isolation and Analysis of the Colorless Salt (Tripotassium Phenolphthalate).

A priori, a salt containing several atoms of potassium replacing the hydrogen of the phenol group would have properties similar to those of an alkali. It would be readily soluble in water, returning in part

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to the colored salt, soluble in alcohol with the splitting off of alkali to form alkaline alcoholates and the colored compound, but insoluble in ether and benzene, etc. In short, we believed the colorless salt would decompose into the colored as soon as excess alkali was removed; and for this reason we did not make any systematic attempt to isolate it.

Accidentally,[1] however, we found certain conditions under which a copious microcrystallin precipitate of the salt could be obtained. Upon microscopic examination, the crystals are revealed as colorless rhomboidal plates, which rapidly assume small, discrete, superficial areas of color, giving the mass, when viewed macroscopically, a pinkish tinge. On careful heating they lose water and their crystallin form, taking on an intense opaque purple color (the dibasic salt; see salt of Mayer[2] and Spengler) with a bronze iridescence, simulating in luster crystals of potassium permanganate. They retain their purple shade on cooling in the absence of moisture, but on exposure to air fade, by passing through various tones of red, to lighter colors, after which they deliquesce. Under ordinary conditions, the almost colorless salt is fairly stable, showing a slight pink tinge only. The crystals are insoluble in ether, benzene or acetone, slightly soluble in amyl alcohol, but in water or ethyl alcohol, they dissolve rapidly, and with the production of very little color, especially if the temperature be kept at 0°. Upon long standing or boiling, however, the aqueous solution develops intense color.

After several purifications, the salt was subjected to different methods of analysis, the results being consistent with the formula $C_{20}H_{12}O_4K_3(OH) + 5H_2O$.

Found:	C, 44.40; H, 4.37; K (six determinations),	21.77.
Calculated:	C, 44.38; H, 4.28; K,	21.73.

Although the average of the determinations of potassium was in close agreement with the theoretical, the individual values varied considerably, as illustrated by the determinations enumerated below.

As a confirmation of our work, we obtained the theoretical amount of phenolphthalein ($C_{20}H_{14}O_4$) from our colorless salt both by precipitation, and by comparing the amount of color with that of a freshly prepared standard solution of phenolphthalein. In both cases the results showed that the salt, on long standing in acid solution or on heating in an acid solution, yielded the theoretical amount of phenolphthalein.

0.1445 gram salt lost, upon heating at 150° C. in air oven, 0.014 gram = 9.7 per cent.[3] Titrated with 0.1 *N* acid: required 7.6 cc. = 0.0297 gram of potassium,

[1] It is our intention to publish the details of the isolation and purification of the salt, together with other items on this subject, in a future paper.

[2] Meyer and Spengler, *Ber.*, 38, 1318; 41, 2446.

[3] This amount of water represents about three molecules of water of crystallization only, the remaining two being probably in combination with alkali, as potassium hydrate.

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= 20.6 per cent.[1] The solution was boiled, rendered alkaline, and diluted to 250 cc.; and the amount of color compared with a solution of standard color. This gave a molecular weight of 548, the theoretical being 540.

1.103 grams of the salt; dissolved in water; titrated with 0.1 *N* hydrochloric acid and heated to split off all the alkali. Total amount of acid required: 61.6 cc.; equivalent to 22.07 per cent. of potassium. The precipitate of phenolphthalein was collected on a Gooch crucible and weighed. The filtrate was evaporated and weighed as potassium chloride.

	Found.	Theoretical.
Phenolphthalein, 0.6427 gram.....	58.3	58.8
Potassium, as KCl, 0.4679 gram.....	22.2	21.7
Hydroxyl and water (by difference).....	19.5	19.5

The preceding results leave no doubt in our minds but that our compound is the tribasic salt of phenolphthalic acid. The isolation of *phenolphthalic acid*, or any of its salts, except the tribasic, presents great difficulties, but we believe that we have developed a method of preparing the monobasic salt. This method has not, as yet, however, been successful as to the process of purification.

(5) Discussion of Results.

Baeyer[2] showed that phenolphthalein has a lactone structure, and it was assumed that sodium hydroxide split the lactone ring and neutralized the resulting acid group. In 1893, Friedlander[3] assumed that the red salt was dibasic, but not until 1905 was it actually demonstrated[4] that it contained two atoms of alkali. Since then, nearly all investigators have agreed that the alkali combines with phenolphthalein with the resulting formation of a quinoid group. This latter is assumed to be the chromophore,[5] or at least a part of it. Meyer and Marx[6] demonstrated that the production of color was incident to a molecular rearrangement with the formation of this group.

According to the preceding explanation, the disappearance of color, upon the addition of an excess of alkali, was assumed to be caused by the destruction of the quinoid ring. As this was believed to occur in strong alkali only, most investigators considered the fading of the colored salt, in dilute alkaline solution, to be due solely to hydrolysis. *Our figures, however, show that hydration begins with the smallest amount of alkali.*

Baeyer, K. Meyer, and A. Hantzsch[7] believed that the colorless salt was formed by the addition of another molecule of alkali. Our experi-

[1] This titration is low, because it was not until later that we realized that it required longer than a few hours for the last traces of tribasic salt to be decomposed.

[2] Baeyer, *Ann.*, 202 (1880).

[3] Friedlander, *Ber.*, 26, 172.

[4] Meyer and Spengler, *Ibid.*, 38, 1318; 41, 2446.

[5] Stieglitz and Acree, *Am. Chem. J.*, 39, 543, 650 and 651.

[6] Meyer and Marx, *Ber.*, 40, 3603.

[7] A. Hantzsch, *Ber.*, 40, 3481 (1907).

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ments and analysis of this new compound point unmistakably to this view. In fact all investigators of the subject, except Ostwald and a few others, who believe it to be a dissociation phenomenon, agree that the colorless modification is due to the addition of alkali. Rohland holds, however, that the ions are colored and the associated molecules colorless; Acree on the other hand does not believe it to be dissociation because the fading requires time. We can conceive of dissociation not occurring instantaneously, hence the time factor would not, of necessity, be a proof against dissociation. The fact that the color fades to an equilibrium, and that the fading is a function of the amount of alkali, would point to the ionization theory. According to the supporters of the ionization hypothesis, the reaction or dissociation is as follows:

$$O\text{—}COC_6H_4C(C_6H_4OH)_2 \rightleftarrows HOOC\text{—}C_6H_4.C\text{—}C_6H_4OH:C_6H_4:O$$

colorless molecule.

$$O:H_4C_6:HOH_4C_6\text{—}C\text{—}H_4C_6COO^- + H^+$$

colored ion.

According to the work of Nietzki[1] and Burckhardt, Nietzki[2] and Schroeter, Green,[3] and King,[3] Bistrzyckis,[4] and others, the color can not be ascribed to the ion, but to the quinoid character of the compound. Stieglitz, and also Meyer and Spengler, pointed out that the dry dibasic salt is highly colored. We have prepared this colored compound from absolute alcohol and sodium ethylate and found it to have intense color and metallic luster. According to Stieglitz, McCoy, and Hildebrand the indicator functionates as monobasic acid, but Wegscheider[5] employed the following equation (dibasic acid) in determining the dissociation of phenolphthalein

$$OCOC_6H_4C(C_6H_4OH)_2 \rightleftarrows HOOCC_6H_4C\text{—}C_6H_4OH:C_6H_4:O$$

$$O:H_4C_6:HOH_4C_6\text{—}C\text{—}C_6H_4COO^- + H^+$$

$$H^+ + O:H_4C_6:\bar{O}H_4C_6C\text{—}C_6H_4COO^-$$

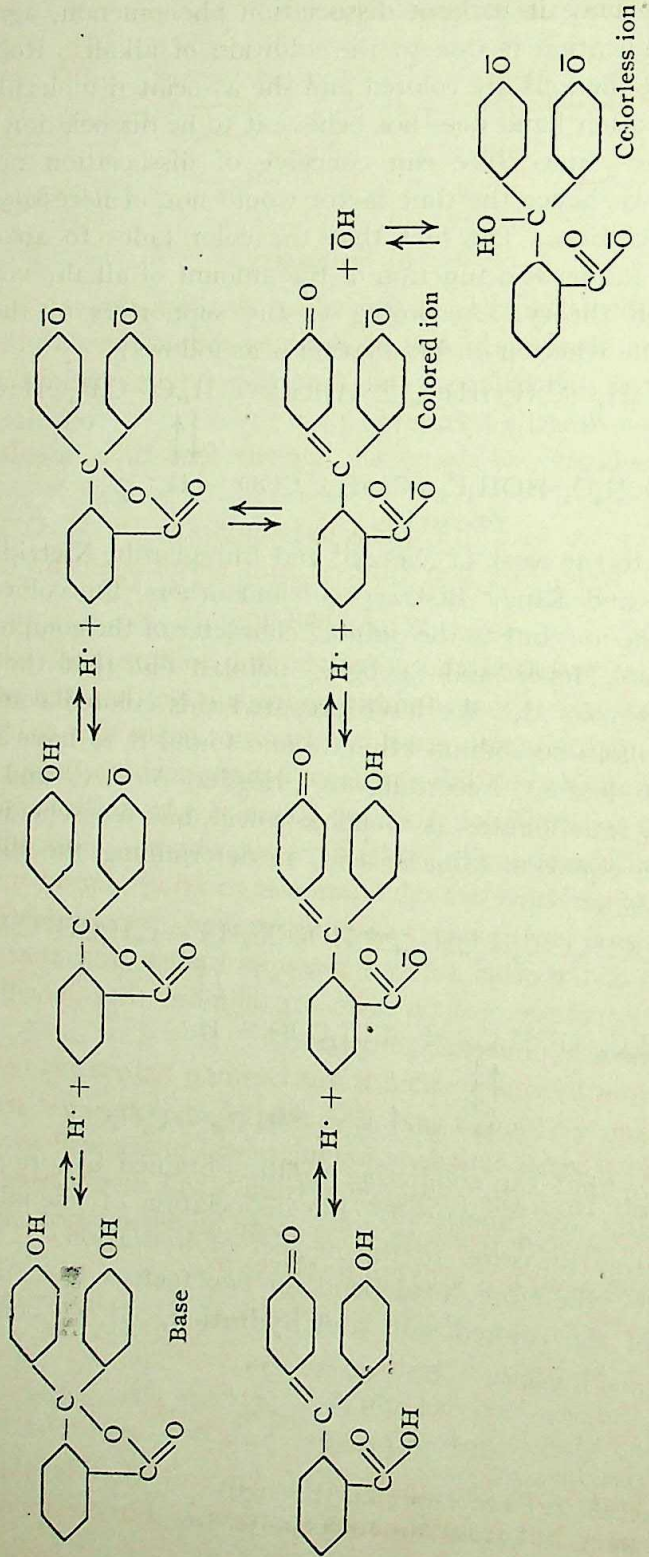
We believe that the conflicting results obtained by previous workers[6] in determining, colorimetrically, the dissociation of phenolphthalein are due, in a large measure, to the neglect of hydration. The amount of color appears, therefore, to depend on two factors, *i. e.*, dissociation or hydrolysis of the colored salt, and hydration. If we consider the hy-

[1] Nietzki and Burckhardt, *Ber.*, 30, 172–178.
[2] Nietzki and Schroeter, *Ibid.*, 28, 48.
[3] Green and King, *Ibid.*, 40, 3724.
[4] Bistrzyckis, *Ber.*, 36, 3558.
[5] Wegscheider, *Z. Elektrochem.*, 14, 510 (1904).
[6] Quoted by A. A. Noyes, THIS JOURNAL, 32, 816.

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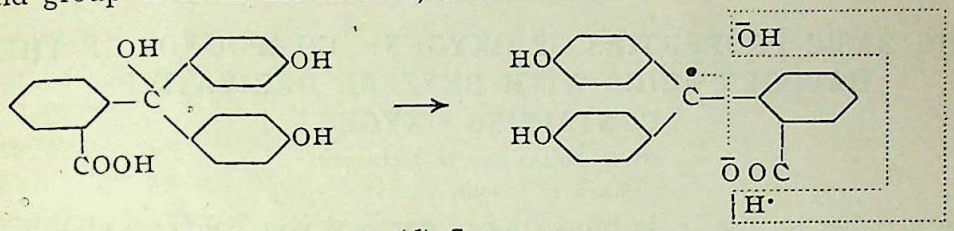
dration from the ionic view-point, phenolphthalein on solution in alkali may be represented as passing through the following stages:



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According to this method of writing the equation, phenolphthalic acid has a strongly alkaline group which, when dissociated, neutralizes the acid group to form the lactone, thus:



(6) Summary.

We have shown that beside *the fading, due to hydrolysis of the dibasic phenolphthalein, there is also that produced by hydration* (with the formation of alkaline phenolphthalates) and that therefore phenolphthalein is not an accurate colorimetric standard.

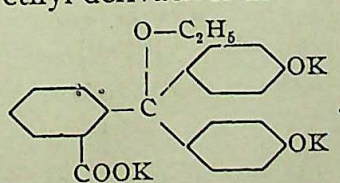
We have isolated and described, for the first time, a salt of phenolphthalic acid.

In conclusion we wish to express our thanks to Dr. H. C. Fleming and to Dr. W. G. Lyle, for their interest and encouragement in this work.

(7) Addendum.

We have also prepared the corresponding sodium salt, which crystallizes in cubes, and is considerably more soluble than the potassium derivative, but otherwise very similar. In order to see that the physiological action of our salts were different from other phenolphthalein derivatives, we submitted to Professor Abel, of Johns Hopkins University, some of our potassium compound. Professor Abel, who has most kindly studied its behavior when injected subcutaneously in dogs, found that there was little evidence of local pain or swelling at the point of injection, contrary to the action of the other salts of phenolphthalein and that it produced purgation. For these reasons, we are hopeful that it will fill the need that exists for a hypodermic purgative.

Our attention has been called to the German Patent 223,968, granted to Farbenfabriken v. Baeyer and Co., August 7, 1910, for *weakly colored, alkaline salts of phenolphthalein*, having useful pharmacological properties. Surmising only from the preparation from alkali alcoholates and the evolution of alcohol upon heating, these compounds are not simple salts of phenolphthalic acid, but ethyl derivatives as



It is obvious from the analysis of our salt that it was not prepared from alcoholates, but from aqueous solutions. Furthermore, we obtained

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large amounts of *perfectly colorless crystals*, which have remained unchanged for several months.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF THE HALOGEN ACIDS WITH BENZENE DERIVATIVES CONTAINING OXYGEN

By O. Maass and D. McIntosh.

Received October 24, 1910.

In a paper on the basic properties of oxygen[1] von Baeyer and Villiger say: "While the substitution of positive groups, such as the alkyls, for the hydrogen in water makes the oxygen basic this is not the case with negative groups like phenyl. Phenyl, benzophenone, etc., do not give salts with acids. This is in full agreement with the behavior of ammonia derivatives, etc."

This generalization is not justifiable, for we shall show in this paper that benzophenone and other oxygen substances containing the phenyl group form complexes almost as readily as do ether, ketone,[2] etc.

Archibald[3] has made an extended study of the electrical conductance of organic compounds dissolved in the halogen hydrides, and in our effort to produce additive compounds we have been largely guided by his results; for it appears almost certain that conduction of organic substances in liquefied hydrobromic or hydrochloric acid is brought about by their union with the acid and the subsequent ionization of the compound. High conducting power in general means the formation of a large amount of the compound, and under proper conditions these addition products may be separated and analyzed.

Experiments with Hydrogen Bromide.—Nitrobenzene, phenol, anisol, phthalic acid, hydroquinone, and pyrogallol are only slightly soluble in liquefied hydrobromic acid, and under the conditions of experiment give no compounds. Benzoin, the cresols, thymol, salicylic acid, naphthol and benzyl alcohol are soluble and probably form compounds in solution, which, however, could not be separated, Resorcinol, benzophenone and benzoic acid give compounds which crystallize readily. They are all colorless substances with sharp melting points well above that of hydrobromic acid (— 86°) and they form supersaturated solutions.

Resorcinol compound, melts —71°; analyses—sample I, 77.8 and 76.8 per cent. acid; sample II, 75.6 and 77.4 per cent. acid. $C_6H_4(OH)_2\,4HBr$ contains 74.6 per cent. acid.

Benzoic acid compound, melts —44°, 56.7, 59.0, 56.4 per cent. acid was found. $C_7H_6O_{22}HBr$ contains 57.2 per cent.

[1] *Ber.*, 33, 1438 (1900).

[2] Walker, McIntosh and Archibald, *J. Chem. Soc.*, 85, 1098 (1904). Vorländer, *Ann.*, 341, 1 (1905).

[3] This Journal, 29, 665, 1416 (1907).

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Benzophenone compound, melts —42°, showed 73.5, 72.7, 75.0 71.5 per cent. acid. $(C_6H_5)_2CO6HBr$ has 72.8 per cent.

Experiments with Hydrogen Chloride. Nitrobenzene, benzoin, anisole, phenol, phenetol, benzoic, phthalic and gallic acids are insoluble or sparingly soluble in liquefied hydrochloric acid. Thymol, salicylic acid, naphthol (α and β) benzyl alcohol, benzaldehyde and cresol are soluble and probably form compounds, but these were not obtained as solids. Resorcinol and benzophenone gave compounds melting below —85°. The resorcinol complex contained about 52 per cent. acid, which corresponds to three or four molecules of hydrogen chloride to one of resorcinol. The benzophenone hydrochloride contained 56.8 per cent. acid while $(C_6H_5)_2CO.7HCl$ has 58.4 per cent. The benzophenone compounds differ from the corresponding ones of the fatty series which contain a much smaller proportion of acid. There are, however, indications of simpler addition products.

Ethyl Ether and Hydrobromic Acid unite to form a compound containing one molecule of each substance and here the oxygen has been assumed to be tetravalent. Since on electrolysis in a hydrobromic acid solution the ether moves to the cathode, the ether hydrobromide has been given the constitution $C_4H_{10}O\begin{matrix}H\\ \diagup\\ \diagdown\\ Br\end{matrix}$, its molecular weight, however, being unknown. A second compound, $C_4H_{10}O.2HBr$, probably exists (previous paper) in which, as in some acid salts of dimethyl pyrone, the oxygen may be taken as hexavalent. In the compounds of benzophenone and the halogen acids the latter are present in greater amounts than would be expected were the oxygen tetra- or even hexavalent. While the constitutions of such complexes might possibly be systematized by the assumption of the union of the acid with the carbon[1] it seems better, at present, to class them merely as substances with acid of crystallization.

McGILL UNIVERSITY, MONTREAL.

TWO-COMPONENT SYSTEMS.

PAPER I. ETHER-HYDROBROMIC ACID, ETHER-CHLORINE AND ETHER-BROMINE.

BY D. McINTOSH.

Received October 24, 1910.

While studying the compounds formed by organic substances containing oxygen with the halogens and with the halogen hydrides, I found it necessary to map out completely or in part several of these two-component systems. The results of three are given in the following pages.

The freezing-point determinations were made in a modified Beckmann apparatus with a platinum stirrer and a pentane thermometer, graduated

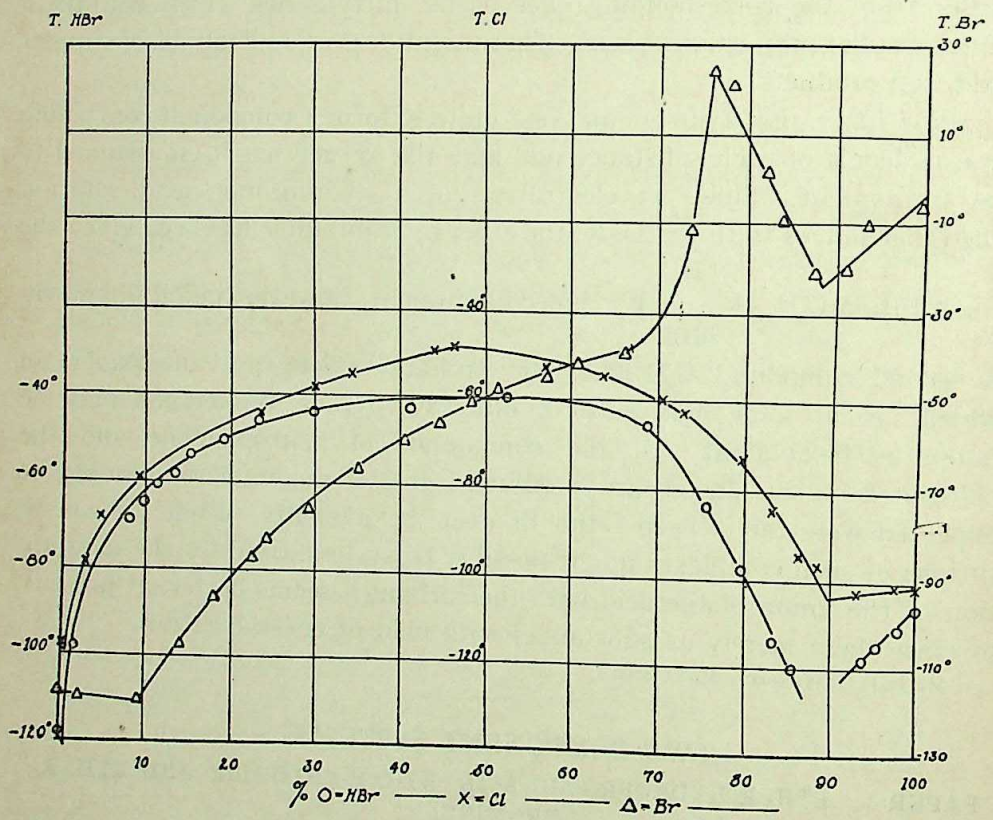
[1] Gomberg, *Ann.*, 370, 142 (1909).

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in degrees and calibrated by means of a constant volume hydrogen thermometer. The temperatures were read to 0.5°; but owing to the sluggish way in which the pentane thermometer reaches equilibrium as well as to its other inherent disadvantages—drops of liquid adhering to the glass—the measurements are accurate only to one or two degrees.

Above —78° carbon dioxide was used as a refrigerant. Between —78° and —108° the solutions were kept at constant temperature by evaporating the carbon dioxide under reduced pressure, and portions were removed for analysis from time to time. The points on this part of the curve are probably much more nearly correct than at higher temperatures. Finally, the few points below —108° were obtained in a smaller Beckmann apparatus cooled by liquid air.



Ether–Hydrobromic acid. — The results of experiments with these substances are given in Table I and shown in the diagram. Ether freezes at —118°. The addition of hydrobromic acid lowers the freezing point slightly, then the compound $C_4H_{10}O.HBr$ separates out, and further addition of the acid raises the melting point giving the curve for the equilibrium between vapor, solution and solid ether hydrobromide. At —40° the ether hydrobromide melts. On adding more of the acid the freezing point falls until the eutectic point is reached, where solid hydrobromic

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acid and compound separate. This occurs at about —115° and the liquid contains 12 per cent. ether. The freezing point then rises with the addition of acid to —86°, the melting point of pure hydrobromic acid.

During these determinations two interesting facts were observed. When more ether than is required to form the compound $C_4H_{10}O.HBr$ is present, the liquid supercools and separates into two layers, the lower containing nearly all the hydrobromic acid. By adding a crystal of the solid compound supercooling may be prevented.

Analyses of the solid separating when over 70 per cent. of acid is present indicate that a compound containing two molecules of acid to one of ether is formed. The percentages are 70.7, 72.5, 67.0, 67.1 and 73.5 acid for compounds made at different times. $C_4H_{10}O.2HBr$ contains 68.7 per cent. acid. The substance obtained melts at —46° but the freezing-point curve shows no break at this temperature.

Hydrobromic acid and ether apparently give two compounds, $C_4H_{10}O$–HBr[1] and $C_4H_{10}O.2HBr$, and in the latter the oxygen may be regarded as hexavalent. An analogous combination was noticed in the case of dimethylpyrone.[2]

TABLE I.

Per cent. acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
0	—118°	41.3	— 43°
1.60	— 98°	52.5	— 40°
2.18	— 92°	68.7	— 46°
3.00	— 79°	75.8	— 64°
8.20	— 69°	79.8	— 78°
9.80	— 65°	83.5	— 94°
11.5	— 61°	85.7	—100°
13.5	— 58.5°	94.0	— 98°
15.4	— 54°	95.5	— 95°
19.4	— 50.5°	98.0	— 91°
23.4	— 46°	100.0	— 86°
29.9	— 44°		

Ether–Chlorine.—The results for this system are shown in Table II and in the diagram. Ether and chlorine form the compound $C_4H_{10}OCl_2$[3]. The first part of the curve shows the equilibrium of the ether-dichloride with solution and vapor. At —51° the compound melts. Further additions of chlorine lower the melting points to —103°, a quadruple point, where solid chlorine, $C_4H_{10}OCl_2$ solution, and vapor are in equilibrium. Pure chlorine melts at —101.5°.

[1] Archibald and McIntosh, *J. Chem. Soc.*, 85, 919 (1904).

[2] THIS JOURNAL, 32, 542 (1910).

[3] *J. Chem. Soc.*, 87, 784 (1905).

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TABLE II.

Per cent. chlorine.	Freezing temperature.	Per cent. chlorine.	Freezing temperature.
0	—118°	57.3	— 53°
3	— 99°	64.1	— 55°
5	— 89°	71.3	— 60°
9.5	— 80°	73.2	— 63°
18.3	— 71°	80.0	— 74°
19.2	— 70°	83.6	— 85°
23.8	— 65°	86.6	— 95°
30.0	— 58°	88.6	— 97°
34.8	— 55°	93.2	—103°
44.3	— 50°	97.8	—101.5°
46.5	— 49	100.0	—101.5°

Ether–Bromine.—These substances unite to form $C_4H_{10}OBr_2$.[1] The addition of bromine to ether depresses the freezing point of the latter and at —119.5° solid ether and ether-dibromide separate. The ether-dibromide melts at —38° and the addition of bromine raises the melting point, the compound $C_4H_{10}OBr_3$[2] being formed. This substance melts at +23°. On adding more bromine the freezing point falls and at —20°, bromine and the tribromide separate. These results are shown in Table III and in the diagram.

TABLE III.

Per cent. bromine.	Freezing temperature.	Per cent. bromine.	Freezing temperature.
0	—118°	57.3	—45°
2.6	—119°	60.8	—42°
9.6	—119.5°	66.4	—40°
14.4	—107°	68.4	—38°
18.4	— 96°	74.1	—12°
23.0	— 87°	76.4	+23°
24.6	— 82.5	78.6	+20°
29.5	— 75.0°	82.7	+ 0.5°
35.6	— 66°	84.6	—10°
40.8	— 59.5°	87.8	—21°
44.9	— 56°	91.5	—20°
48.6	— 51°	94.0	—11°
51.8	— 48°	100.0	— 7°

Above —40° the measurements are difficult to make with any degree of accuracy. Substitution of the bromine in the ether may begin and I have never succeeded in obtaining the tribromide without several per cent. of hydrobromic acid. The dibromide can be made with less than 1/20 per cent. acid. It may be pointed out that the phenomena[3] observed by Plotnikov and others—conduction of the ether-bromine mix-

[1] *J. Chem. Soc.*, 87, 784 (1905).
[2] Schützenberger, *Ann.*, 129, 50 (1864).
[3] Johnson and McIntosh, THIS JOURNAL, 31, 1138 (1909).

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ture and its action on metals, etc.—are probably due to the hydrobromic acid formed rather than to the ether–bromine compounds.[1]

Further work on similar systems at low temperatures is being done in this laboratory.

McGill University, Montreal.

[Contribution from the Laboratory of Soil Fertility Investigations.]

METHOXYL IN SOIL ORGANIC MATTER.[2]

By Edmund C. Shorey and Elbert C. Lathrop.

Received October 13, 1910.

The fact that the quantity of organic matter in different soils varies has been so well established that it is common knowledge. On the other hand the fact that the organic matter of soils varies widely in kind, that two soils may contain the same quantity of organic matter and this material be made up of quite different organic compounds in each case, while quite easily demonstrated, has not received general recognition.

The prevailing ideas regarding humus and humus formation seem to be based on the assumption that the multitude of organic compounds of many types present in the dead vegetation that contributes to the formation of the organic matter of soils is in some mysterious way reduced in the process of decay to a few compounds of the same type. The first step toward showing that this assumption is unwarranted is taken when it can be shown that soil organic matter varies greatly in the kind or types of organic chemical compounds comprising it. This can be shown in a number of ways, but the methods used can be classed under two general heads: first, the isolation of a number of definit organic compounds of different types; second, the application of group or class reactions that disclose the presence or absence of certain groups of organic compounds.

Under the first head much work has been done and has already been reported.[3] In this work the demonstration of the variability in kind of organic matter has been incidental to the broader investigation of the chemical nature of this material.

In the use of type or group reactions the application may be simply a qualitative one, or where the reaction is of a character to permit it, may be quantitative. A reaction that may be used in this way is the formation of methyl iodide when compounds in which there is a methoxyl group, CH_3O, are treated with concentrated hydriodic acid. The method

[1] Note.—Carefully dried ether and bromine (75 per cent. Br) had at —30° a resistivity of 1000 ohms; then chemical action commencing the temperature rose and in a few seconds the resistance had fallen to 7 ohms.

[2] Published by permission of the Secretary of Agriculture.

[3] *Bulls.* 53 and 74, Bureau of Soils, U. S. Dept. Agr. This Journal, 30, 1295, 1599 (1908); 31, 116 (1909); 32, 1674 (1910). *J. Biol. Chem.*, 8, 381 (1910).

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for the quantitative determination of the methoxyl radical by this reaction was first suggested by Zeisel, and is generally known as the Zeisel[1] method. A number of improvements and modifications of the apparatus used have been suggested,[2] but the method as originally described is still in general use.

The first and only application of this method to organic material derived from soils is found in a paper on the chemistry and physiological action of the humic acids, in which Robertson, Irvine and Dobson[3] reported investigations into the chemical composition and constitution of humic acids. These authors obtained four preparations of humic acid—two natural from peat by treatment with ammonium and potassium hydroxide respectively, and two artificial by boiling sugar with hydrochloric acid and treating portions of the brown amorphous material so obtained with ammonium and potassium hydroxide. They found some difference in composition of the natural preparations that obtained through ammonia containing 54.24 per cent. carbon, while that through potassium hydroxide contained 56.67 per cent. The artificial preparations were almost identical in composition except that the one obtained through ammonia contained 0.76 per cent. nitrogen, while the other was nitrogen-free. In these preparations the authors determined methoxyl, CH_3O, by the Zeisel method, and found such a wide difference between the natural and artificial preparations in this respect, that the only conclusion justified is that there are important differences in constitution, despite the general agreement of properties and composition. In the humic acid from peat 1.71 to 2.47 per cent. CH_3O was found while in that from sugar 6.47 was obtained.

In the application of this method to soils reported here, ten soils of widely different types and organic content, the same used in the pentosan determinations discussed elsewhere,[4] were used. In making the determination five grams of air-dried soil were used except in cases where the organic content was very low, when ten grams were used. Ten cubic centimeters of hydriodic acid, sp. gr. 1.7, were added and the determination carried out in the manner originally described by Zeisel. The results obtained were calculated to the basis of the soil dried at 105° and the figures given are the mean of closely agreeing duplicates. In the case of the North Carolina peat, No. 4, and the Marshall loam, No. 5,

[1] *Monatsh. Chem.*, 6, 989 (1885); 7, 406 (1886).

[2] Benedict and Grüssner, *Chem.-Ztg.*, 13, 872 (1889). Ehmann, *Chem.-Ztg.*, 14, 1767 (1890). Benedict and Bamberger, 15, 221 (1891). Perkin, *Proc. Chem. Soc.*, 13, 239 (1903). Herzig, *Monatsh. Chem.*, 9, 554 (1888). Bamberger, *Monatsh. Chem.*, 15, 505 (1894). Gregor, *Monatsh. Chem.*, 19, 116 (1898). Kaufler, *Analyst*, 27, 126 (1902).

[3] *Biochem. J.*, 2, 458 (1907).

[4] THIS JOURNAL, 32, 1680 (1910).

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in the table, there was a slight darkening of the silver iodide precipitate due, no doubt, to the evolution of hydrogen sulfide by the action of the acid on the soil, and the consequent formation of silver sulfide. Separation of the silver sulfide gave quantities too small to weigh, and while the figures for these soils may be high the error can be but slight.

The results obtained and calculations made therefrom are presented in the following table.

METHOXYL IN SOILS.

	Per cent. total carbon.	Per cent. CH_3O.	Per cent. methoxyl carbon.	Methoxyl carbon per 100 total carbon.
1 Elkton silt loam	0.522	none	.....	.....
2 Sassafras silt loam	0.315	0.003	0.001	0.317
3 Chester silt loam	1.510	0.004	0.001	0.066
4 N. Carolina peat	27.102	1.114	0.431	1.590
5 Marshall loam	6.971	0.131	0.050	0.717
6 Cal. peaty soil	11.478	0.027	0.010	0.087
7 Norfolk fine sandy loam	0.822	none	.....	.....
8 Santa Paula Cal. loam	1.308	0.004	0.001	0.076
9 Portsmouth loam	3.854	0.006	0.002	0.051
10 Susquehanna clay loam	1.048	0.002	0.0007	0.066

It will be noted that two soils contain no methoxyl; that soils Nos. 3, 8, 9 and 10 gave figures for the ratio methoxyl carbon to total carbon approximately the same, while soils Nos. 2, 4, 5 and 6 gave a much higher ratio. The Elkton silt loam and the Sassafras silt loam soils Nos. 1 and 2 are geologically of the same origin, of the same mechanical and mineral composition, and contain approximately the same quantities of total organic matter, but the former contains no methoxyl while the latter stands third in the ratio of methoxyl carbon to total carbon. On the whole the figures are sufficient to warrant the conclusion that the quantity of methoxyl bears no constant relation to the total organic matter. In other words the soil organic matter varies with respect to the compound or compounds containing the methoxyl radical.

The methoxy group, CH_3O, is found in a large number of organic compounds of very diverse origin. Many alkaloids contain this radical and its determination by the Zeisel method has aided materially in establishing the constitution of some of these compounds. Among the more important alkaloids quinine[1] and codeine[2] contain one and brucine[3] two methoxyl groups.

A number of essential oils contain the methoxyl radical usually in a methyl ester of a substituted phenol. Thus anise oil contains anethole,

[1] Hesse, *Ann.*, 205, 314 (1880). Lipmann and Fleissner, *Monatsh. Chem.*, 16, 34 (1895).

[2] Herzig and Meyer, *Monatsh. Chem.*, 15, 613 (1894).

[3] Zeisel, *Monatsh. Chem.*, 6, 989 (1885). Shenstone, *J. Chem. Soc.*, 43, 101 (1883).

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$C_3H_5.C_6H_4OCH_3$, oil of cloves, eugenol, $C_3H_5C_6H_3(OCH_3)OH$, and oil of parsley, apiole, $C_3H_5C_6H(OCH_3)_2 : O_2 : CH_2$.

From the point of view of the origin of this radical in soil organic matter its occurrence in woody tissue is most important. Benedict and Bamberger[1] determined the methoxyl in a large number of woods and found it to be fairly constant, the methoxyl calculated as CH_3 was usually between two and three per cent., the extremes being 1.99 and 3.21 per cent., and they suggested this determination as a method of arriving at the quantity of wood cellulose in a mixture such as paper. It has been found that methoxyl is always a constituent of the lignocellulose or so-called compound cellulose of higher plants but the quantity in grasses, shrubs, etc., varies much more than in woods.

With these three sources of methoxyl compounds in mind it is clear that in the death and decay of vegetation all soils are having added to them organic material containing this radical. The fact that the quantity of methoxyl in soils varies and bears no relation to the total organic matter is no doubt due in part to variation in the composition of the vegetation that is the source of the organic matter, but the fact that it persists or forms in one soil and disappears in another of the same general type indicates that the processes of decay are quite different in different soils.

The methoxyl group then constituting but a small, and perhaps unimportant, part of the soil organic matter, by its presence or absence, or when present, by its proportion to the total organic matter, demonstrates one form of variation of soil organic matter. This or any other variation when found in soils of the same type and supplied with organic material from the same general source must be regarded as proof of some fundamental difference in the chemical, physical or biological factors that decide in what way a complex organic compound shall break down or decay when added to a soil.

Bureau of Soils, Washington, D. C.

[Contribution from the Laboratory of Soil Fertility Investigations.]

GLYCERIDES OF FATTY ACID IN SOILS.[2]

By Oswald Schreiner and Edmund C. Shorey.

Received October 13, 1910.

The oils, fats and waxes are widely distributed in plants and animals and it follows that considerable quantities of these materials get into the soil and form the material from which soil organic matter is made. From the evidence at hand in the form of substances isolated from soils, it is clear that in some soils, at least, these compounds persist unchanged.

[1] *Monatsh. Chem.*, 11, 260 (1890).

[2] Published by permission of the Secretary of Agriculture.

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The isolated substances represent esters in the form of glycerides and higher alcohols.

The presence of unchanged plant glycerides in the soil is of interest in view of the number of substances of a fatty nature which have already been isolated from soils. In discussing the possible origin of dihydroxystearic acid in the soil, it was pointed out that oleic acid in the form of a glyceride was a nearly universal plant constituent and that it was possible that dihydroxystearic acid might be formed from it in the soil in somewhat the same way as in the laboratory.[1] Cholesterol-like compounds seem to occur frequently in soils[2] and oleic acid or olein may have some relation to the occurrence of this group, inasmuch as Lifschütz[3] has shown that cholesterol compounds may be formed by the oxidation of oleic acid.

The glyceride described in this paper was obtained from the Elkton silt loam as the final step in the treatment which resulted in the isolation of α-hydroxystearic acid and paraffinic acid. So far all soils examined in this manner give at this stage an oily, semi-solid mass similar in appearance to that obtained from the Elkton silt loam. In only a few cases, however, has sufficient material been obtained to establish its identity as a glyceride.

Glycerides of Fatty Acids.—When the alcoholic filtrate from the lead precipitate of paraffinic acid obtained in the isolation of this compound in the manner described in a previous paper[4] is freed from lead by hydrogen sulfide and the alcohol evaporated, there is left an orange-colored oil which remains clear and liquid at room temperature, but becomes turbid on cooling, crystallin material finally separating. This oil on examination proved to be a mixture of glycerides of fatty acids as are most natural oils.

The oil obtained in the manner just described is slightly acid to litmus and has an odor not unlike that of olive oil. Its specific gravity at 26° is 0.935. On saponification with alcoholic potash and evaporation of the alcohol, a soap was obtained completely soluble in water. When the soap solution was acidified with sulfuric acid the fatty acids were set free and extracted by shaking with ether. The mixture of fatty acids obtained on evaporating the ether was a fatty, semi-solid mass from which crystallin leaflets separated on standing. This mass immediately after removal of the ether had an odor suggesting capric acid, but this disappeared in a short time, leaving a tallow-like odor. On shaking the mixed fatty acids with equal parts of nitrosylsulfuric acid and water, a solid mass was obtained on standing, thus showing the presence of oleic acid. The

[1] *Bull.* 53, Bureau of Soils, U. S. Dept. Agr. (1909); THIS JOURNAL, 30, 1599 (1908).
[2] THIS JOURNAL, 31, 116 (1909).
[3] *Z. physiol. Chem.*, 55, 1 (1908).
[4] THIS JOURNAL, 32, 1674 (1910).

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original glyceride behaved in the same manner, indicating the presence of oleic acid or olein in the oil. The presence of oleic acid or at least of some unsaturated acid was confirmed by the fact that the acid mixture when dissolved in carbon tetrachloride decolorized bromine without setting free hydrobromic acid.

In the water solution left after acidifying the soap solution and extracting with ether, the presence of glycerol was shown by the usual tests. The acid liquid was evaporated nearly to dryness and mixed with a small quantity of potassium hydrogen sulfate and the mass so obtained heated in a test tube provided with a stopper and delivery tube which dipped beneath the surface of a few cubic centimeters of water in a second tube. The presence of acrolein in the second tube, as a result of the distillation of glycerol, was established by the characteristic odor and by the generation of a pink color when treated with fuchsin-aldehyde reagent.[1]

The fact then that the oil obtained from the soil is a glyceride is established first by the changed character of the material after saponification and second by the presence of glycerol in the saponification products. It is, of course, possible that there is some free acid present in the oil, but the indications are that such must be small, if any. That the oil is a mixed glyceride is established by the complex character of the fatty acids obtained on saponification, a semi-solid mass from which crystallin material separated, oleic acid also being present.

When the soap solution resulting from the saponification of this oil is dried and extracted with petroleum ether and the ether evaporated, there is obtained a small quantity of unsaponified material. This forms a soft, waxlike mass insoluble in water, but soluble in soap solution. This material gave the Liebermann's cholesterol reaction strongly, but it was not possible to obtain from it any definit crystals of any cholesterol compound.

The oil obtained from the soil is, therefore, a glyceride of fatty acids containing a small quantity of unsaponifiable material and possibly a small quantity of free acid. As such then it corresponds in all particulars with natural glycerides, especially the vegetable oils.

The presence of glycerides similar to natural oils in the soil can perhaps best be explained on the ground that they are unchanged plant residues which have resisted decomposition. Nearly all plants at some stage of their development contain glycerides and they may also be built up by microörganisms as with other plants. They are probably not formed by purely chemical reactions such as are likely to take place in the soil.

BUREAU OF SOILS, WASHINGTON.

[1] A solution of fuchsin decolorized with sulphur dioxide.

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[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

PARAFFIN HYDROCARBONS IN SOILS.[1]

BY OSWALD SCHREINER AND EDMUND C. SHOREY.

Received October 13, 1910.

The paraffin hydrocarbons represent the simplest form of organic compounds and are widely distributed in nature. The lowest member of this group, methane or marsh gas, CH_4, is a constant product of the decomposition of organic matter under certain conditions. Higher members of the group, liquid and solid, occur as mixtures very widely distributed in the earth's crust as petroleum, asphalt, or similar deposits and also in mineral resins. The occurrence of paraffin hydrocarbons in plants is not very common and so far as observed is confined to a few members of the group and to a few species of plants. The large deposits in the earth's crust cannot, then, be attributed to the accumulation of unchanged plant residues; and a great many theories have been propounded to account for these deposits, most of them based on some transformation of organic material.

In spite of the fact that these hydrocarbons are of rather rare occurrence in plants and are seldom added to soil in plant débris, the wide distribution of extensive deposits of such compounds and the occurrence also of mineral resins and shales from which hydrocarbons can be obtained in the rocks from which soils are formed might lead one to expect to find some trace of these compounds in the soil. The question is also raised by this consideration whether some of the processes by which hydrocarbons have been formed from more complex organic compounds may not take place in the soil and escape recognition because the conditions are not favorable for the accumulation of these products in the soil. The production of the simplest paraffin hydrocarbon, methane, is known to take place in soil organic matter when submerged under water, as in swamps. The production here is supposed to be due to the activity of anaërobic microörganisms, but it is not known that absolutely anaërobic conditions are essential to this production or that methane may not be formed in small quantities in ordinary soils. Methane is present in the gases from the combustion of fuel, even when excess of oxygen is available and it has been found in the combustion of organic compounds in elementary analysis that some of the carbon may be present in the products of combustion as methane instead of carbon dioxide, and this when the combustion was carried on in pure oxygen. It may be, therefore, that in the decomposition of organic matter the formation of methane rather than carbon dioxide depends on the structure or constitution of a portion of the material decomposed and similarly more complex members may also be split off

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One paraffin hydrocarbon has been isolated from a soil and while in this particular case there is nothing to indicate that it may not be an unchanged plant residue, the isolation is of interest not only in accounting for a small portion of the organic matter, but also in that it opens up the question of a possible connection between the processes that go on in the soil and the processes by which paraffin hydrocarbons have been formed in nature.

Hentriacontane, $C_{31}H_{64}$.—A peaty soil from North Carolina containing .27 per cent. organic carbon, when extracted with boiling 95 per cent. alcohol yields a dark-colored extract from which on cooling a light yellow microcrystallin substance separates. This material was separated by filtration and the alcohol removed from the filtrate by evaporation, the volume being kept constant by the addition of water. There was formed a reddish-brown precipitate, which after separation and washing was in the form of a brown resinous powder. Extraction of this with boiling petroleum ether yielded a light-colored solution, which after removal of the petroleum ether left a light yellow, oily residue. This was saponified with alcoholic potash, the alcohol removed and the soap dried and extracted with petroleum ether. On evaporation of the petroleum ether the residue was a light-colored, waxy mass completely soluble in a relatively large volume of hot alcohol. On cooling the alcoholic solution thus obtained, there was a separation of a feathery microcrystallin substance which was collected, washed and purified by recrystallizing several times from alcohol.

As thus obtained, the compound was a hard, waxy mass, melting at 68° and having a specific gravity of 0.780 at its melting point. It was soluble in ether and petroleum ether, difficultly soluble in hot and very little soluble in cold alcohol. It was unacted on by fuming nitric acid at room temperature and did not absorb bromine.

The elementary composition as well as its resistance to nitric acid shows it to be a hydrocarbon and its behavior toward bromine that it must be a saturated compound. The melting point indicates hentriacontane. While it is difficult to obtain paraffin hydrocarbons in a condition of absolute purity, an elementary analysis gave the following figures:

	Found.	Calculated for $C_{31}H_{64}$.
Carbon	84.14	85.22
Hydrogen	15.11	14.78

Hentriacontane is a member of the paraffin series found in the paraffin residue of some petroleums. It has also been found in beeswax together with another member of the same series, heptocosane, $C_{27}H_{56}$.[1] It occurs

[1] Schwalb, *Ann.*, 235, 117 (1886).

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also in some plants, having been found in the leaves of *Gymnema sylvestre*,[1] in tobacco leaves,[2] and in East India ko-sam seeds, *Brucea sumatrana*.[3] With this information regarding its occurrence as a natural product and in the absence of any information regarding the possibility of its formation from other soil organic matter, this paraffin hydrocarbon may be regarded as an unchanged plant residue.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

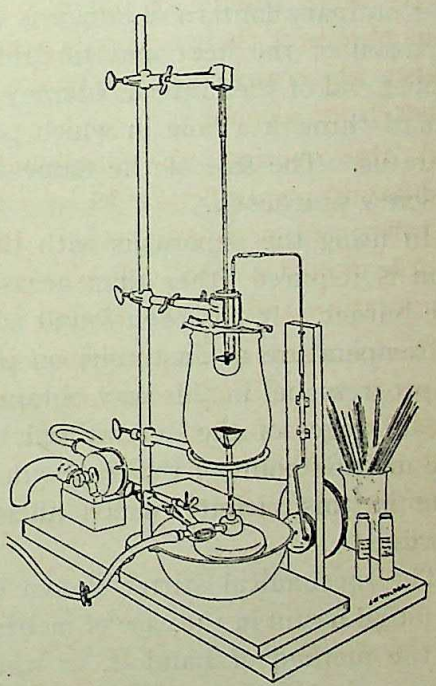
[CONTRIBUTION FROM DIVISION OF PHARMACOLOGY, HYGIENIC LABORATORY, U. S. P. H. AND M.-H. SERVICE.]

CONVENIENT ATTACHMENTS FOR A MELTING-POINT APPARATUS.

BY ATHERTON SEIDELL.

Received November 11, 1910.

In a bulletin[4] of the Hygienic Laboratory entitled "A Study of Melting-Point Determinations," Dr. Geo. A. Menge describes a simplified form of melting-point apparatus which he found, after numerous experiments, to embody all the essential features required for the practical and reasonably accurate determination of melting points. In using the apparatus it was specified that the bath be constantly stirred during the determination and that the heat be applied in such a manner that the rate of rise of the temperature remain constant (3 degrees per min.) over a range of 20° immediately preceding the temperature of melting and at a slower constant rate ($^1/_2$ degree per min.) while the compound was melting. To accomplish this it was necessary to operate the stirrer continually with one hand and the Bunsen burner with the other. Although this cannot be called a difficult feat for most persons it was apparent that a certain amount of skill and practice would be required on the part of some individuals. It was on this account, therefore, that it appeared desirable to devise attachments to operate the stirrer automatically and



[1] Power and Tutin, *Pharm. J.*, [4] 19, 234 (1904).
[2] Thorpe and Holmes, *J. Chem. Soc.*, 79, 982 (1901).
[3] Power and Lees, *Pharm. J.*, [4] 17, 183 (1903).
[4] *Bull.* 70, Hygienic Laboratory, U. S. P. H. and M.-H. Service, Washington, October, 1910.

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provide a source of heat which would not require constant attention. The accompanying illustration shows how these two ends were accomplished with the aid of attachments made from materials on hand in the laboratory.

The melting-point apparatus itself is the one used by Dr. Menge and will be found described in detail in the Bulletin mentioned. The mechanical stirrer as will be seen from the figure consists simply of an upright piece of wood fixed into a solid base; a pulley driven by a small water motor is provided at the lower end of the upright and to the opposite side is attached a rod connected in such a way as to give a perpendicular reciprocating motion. At its upper end, the rod is bored out to about $^1/_2$ inch depth and a diameter slightly larger than the glass tube of the stirrer. The end of the stirrer is placed loosely in this hole and the water motor started when it is desired that the melting-point bath be automatically stirred.

The device for securing the constant source of heat consists of a small-sized Bunsen burner provided with a piece of wire gauze about one inch square fastened in a horizontal position about one inch above the upper end of the burner. This wire gauze serves to spread out the heat and prevent the free flame coming near the bath of the melting-point apparatus. An ordinary lantern chimney is used as a screen for preventing the dissipation of the heat and to protect the flame from air currents. The upper end of the lantern chimney is nearly closed with a piece of asbestos board through a hole in which passes the bath of the melting-point apparatus. The size of the flame of the burner is regulated by means of a screw pinchcock.

In using the apparatus with the attachments as shown no manipulation is required other than occasional adjustment of the pinchcock of the burner. It has been found advantageous to plot the rate of the rise of temperature against time on profile paper while the determination is in progress and in this way obtain a visible record of the rate of heating at all stages of the determination, but especially so for the range near the melting point of the compound, since it has been shown that it is the rate in this vicinity which affects most markedly the melting values obtained.

The mechanical stirrer shown in the illustration will, no doubt, also be found useful in the case of melting-point determinations made according to the method of Landolt, in which a sufficient quantity of the sample to surround completely the bulb of the thermometer is employed. It is also probable that it could be advantageously adapted to the usual forms of apparatus used for the determination of freezing points.

WASHINGTON, D. C.

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NOTES.

Note on the Decomposition of Alloxan.—I recently observed the notes of Professor Wheeler and Professor Bogert in THIS JOURNAL on "The Instability of Alloxan," **32**, 809, and it occurred to me that I should examin a specimen of 10 grams of alloxan which I obtained about a year ago from Kahlbaum.

The neck of the small glass-stoppered bottle was found to be coated with a fine, dry mass varying in color from white to deep red, in spots. This mass had, evidently, been forced out between the glass stopper and the bottle. On attempting to remove the stopper, I found it was firmly fixed in place and the bottle was finally opened by breaking off the neck. When the neck was broken there was a violent puff of gas showing that the contents of the bottle had been under considerable pressure, and it seems probable that if the bottle had not been opened at this time I might shortly have experienced such an explosion as Professor Wheeler reports.

In an examination of the contents of the bottle, a portion taken from near the bottom proved to be unchanged alloxan. The residue of gas in the bottle contained a large amount of carbon dioxide. Of principal interest, however, was the incrustation on the outer surface of the bottle, which was found to consist, chiefly, of urea, oxalic acid and alloxantin.

It would thus appear that the decomposition of alloxan, on standing, proceeds slowly and follows well-known reactions (see Liebig and Wöhler, *Ann.*, **38**, 359 and Strecker, *Ibid.*, **113**, 53) only reaching explosive violence when the carbon dioxide is unable to escape from the bottle. This observation is in accord with the suggestion offered by Professor Franklin, THIS JOURNAL, **32**, 1362.

ROSS AIKEN GORTNER.

THE CARNEGIE INSTITUTION OF WASHINGTON,
COLD SPRING HARBOR, N. Y.

NEW BOOKS.

Progressive Problems in General Chemistry. By CHARLES BASKERVILLE and W. L. ESTABROOKE. Boston: D. C. Heath and Co. 13 × 19 cm., pp. 243. Cloth. Price, $1.00.

This little work consists entirely of a list of problems in chemistry systematically arranged. These problems are in part collected from various sources and in part original. Uniform nomenclature has not been introduced in order that the student may become familiar with the various terms that are actually in use. The book contains quite a number of problems of the same type, so that a selection may be made and the book may be used for a number of years before solutions of the problems may be handed down from one class to another.

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While on the whole the problems are well selected and clearly put, some of them are not sufficiently definit. For example, in problem 64, p. 53, "Find the volume of 10 g. N_2O; 13 g. NO; 7 g. N_2O_3; 6 g. N_2O_4," it ought to be stated under what conditions of temperature and pressure. The same is true of problem 53, p. 52, "Find the mass of 5.6 l. of CO;" also of problems 229 and 235, p. 184. It is probably intended that in working with gaseous volumes standard conditions are to be understood unless otherwise stated; but if so, a statement to this effect ought to be clearly made in some appropriate place.

To the teacher who finds that he can not devise problems in sufficient number for his class this book will be useful, though to be sure he would have to solve each of the problems himself so as to be able to check up the work of the pupil, for answers to the problems are not given in the book.

The volume is neatly bound in cloth and well printed.

LOUIS KAHLENBERG.

Introductory Notes on Quantitative Analysis. By C. W. FOULK, of Ohio State University. Published by the author. 239 pages. 2nd. ed. Price, $2.50.

This book differs from most books on the subject in that it is not devoted to a description of methods or examples of analysis. Over half of the book (130 pages) is given up to general and special directions on manipulation and the discussion of points which come up in quantitative work but which are usually omitted from books on the subject. Some of the points dwelt upon are: Weighing, fusions, precipitation, filtering, washing, sources of error, indicators, titration, normal solutions, calibration of volumetric vessels, etc., etc. While it is doubtful whether all of the explanations are explicit enough to be followed by a beginner, they will serve to call to his attention many points which are ignored by most books and will lead to a thoughtful consideration of the subject. The book is not intended to take the place of the instructor but to aid in giving the student a thorough grounding in the principles of quantitative analysis. The second part of the book (108 pages) is given to the directions for the analysis of fourteen examples. Whether the selection of these examples is the wisest is, of course, a matter for individual determination. Each example is taken as a type and is treated as such and not as an individual substance. Gravimetric, volumetric and electrolytic methods are discussed among the examples.

The contents of the book represent a year's work, classroom and laboratory, in quantitative analysis as carried out in the author's laboratory, and, as notes, have been used by him for a number of years. It is therefore thoroughly usable in all of its parts and will make a very satisfactory text book.

OWEN LOUIS SHINN.

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Van Nostrand's Chemical Annual: Second Issue, 1909. Edited by J. C. OLSEN. New York: D. Van Nostrand Company. Price, $2.50 net.

The first issue of this valuable book has already been reviewed (THIS JOURNAL, **29**, 947 (1907)). In the present issue some new features are introduced, such as, for example, tables of the physical constants of the alkaloids and of the essential oils and a table of data relating to fusible alloys. In response to numerous changes in the accepted values of the atomic weights, the necessary recalculations have been effected. The tables of physical constants of inorganic and organic compounds, which are, of course, the most extensive single items, have not simply been reprinted. In common with all the other contents, they have been thoroughly revised, and have been largely modified by the inclusion of recently determined values. The selected lists of original papers and of books, which contain the titles of publications appearing since the first issue went to press (July, 1906), occupy over one hundred pages. No pains have been spared to bring the work up to date. The editor and publishers are to be congratulated on the well merited success which has attended the publication of the Annual. No chemist can afford to be without this edition.

ALEXANDER SMITH.

RECENT PUBLICATIONS.

AUSTEN, W. C.: **Introduction to the Study of Metallurgy.** Sixth edition. London: 8°, 494 pp., 18.50 M.

BÄCKLUND, A. V.: **Zur Theorie der Fluorescenz.** Berlin: R. Friedländer & Sohn. 30 pp., 1 M.

BAMBERGER, M.: **Ueber die Geschwindigkeit chemischer Reaktionen.** Wien: 8°, 60 pp., 2 M.

BAUER, F.: **Tabellen zum direkten Ablesen der Sudhausausbeute.** München: R. Oldenbourg, 130 pp., 6 M.

BAUMHAUER, N.: **Leitfaden der Chemie. 2 Teil. Organ. Chemie.** 4 Aufl. Freiburg: Herder'sche Verlagshandlung, 1.80 M.

BECKER, G. A.: **Ueber den Zusammenhang zwischen Farbe und Konstitution der Pyridinfarbstoffe aus sekundaren Aminen.** Dresden: Thomas & Hubert, 57 pp.

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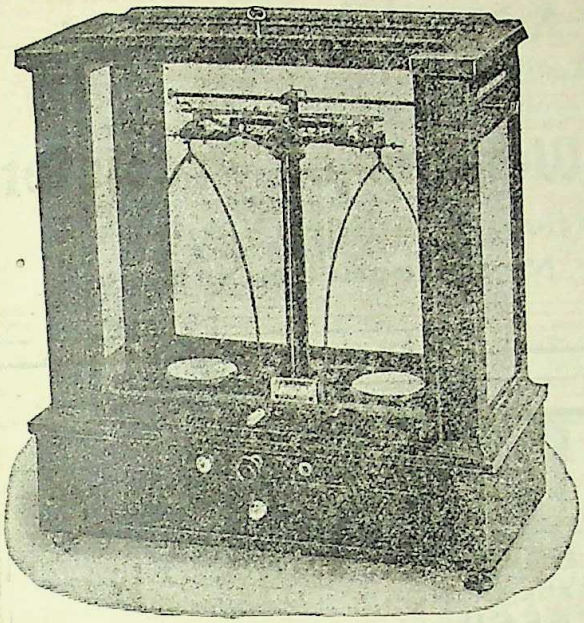
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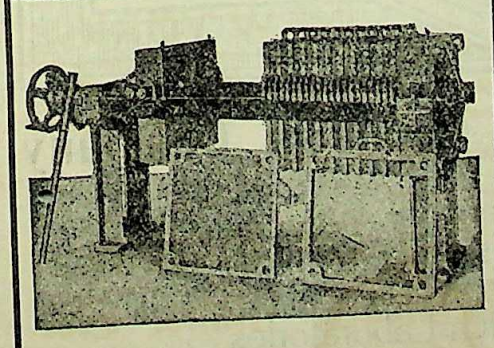
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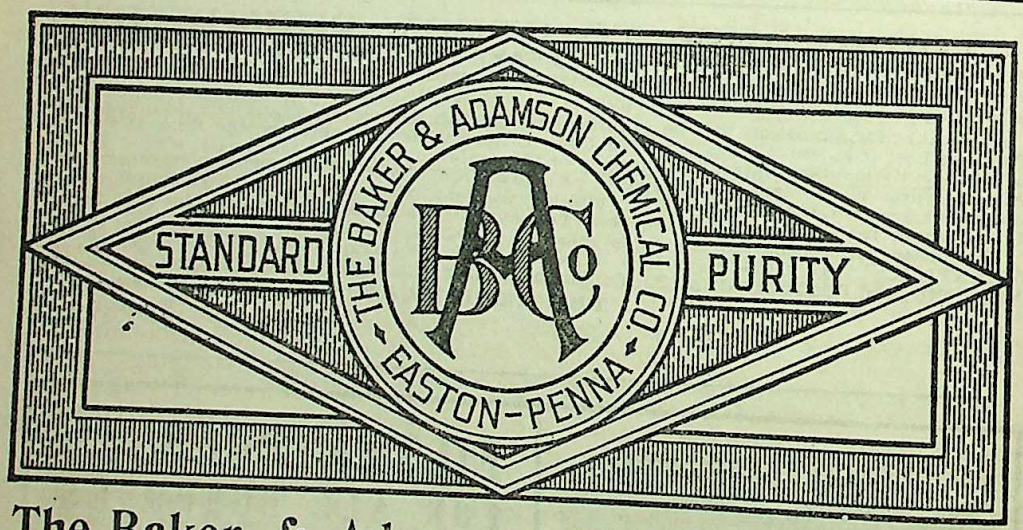
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Cellulose. The Cellulose Nitrates (Theory). Nitration of Cellulose (Practice). Cellulose Nitrate Solvents and Non-Solvents. Fusel Oil, Natural and Synthetic. Amyl Alcohols. Manufacture and Properties of Amyl Acetate, Natural, Artificial, Synthetic Camphor. Camphor Substitutes. Paint Removers. Turpentine Substitutes. Pyroxylin Solutions. Pyroxylin Lacquers. Bronzing Liquids. Waterproofing Compositions. Artificial Leather, Skin, Fur, Feathers, Rubber, Pyroxylin-Coated Leather and Splits. Patent and Enameled Leather. Celluloid, Pyralin, Xylonite, Viscoloid. Pyroxylin Plastics Celloidin and Cellulose Nitrates in Microscopy. Collodion and Cellulose Nitrates in Pharmacy, Medicine. Film Manufacture and Photography. Artificial Silk, Whalebone, Gorse, Horsehair. The Cellulose Acetates. Guncotton and the Explosive Cellulose Nitrates. Viscose, Viscoid, and the Cellulose Xanthates. Denatured Ethyl Alcohol. Patent, Author, and Subject Index.

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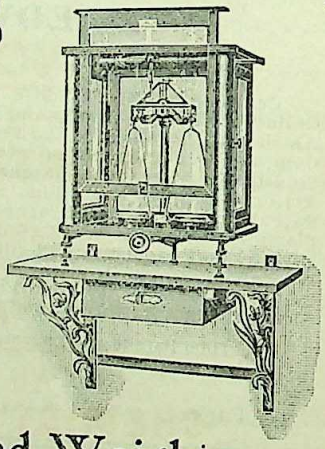
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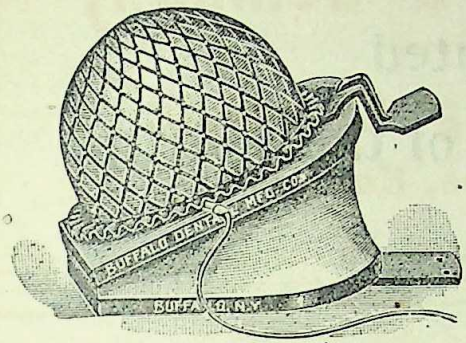
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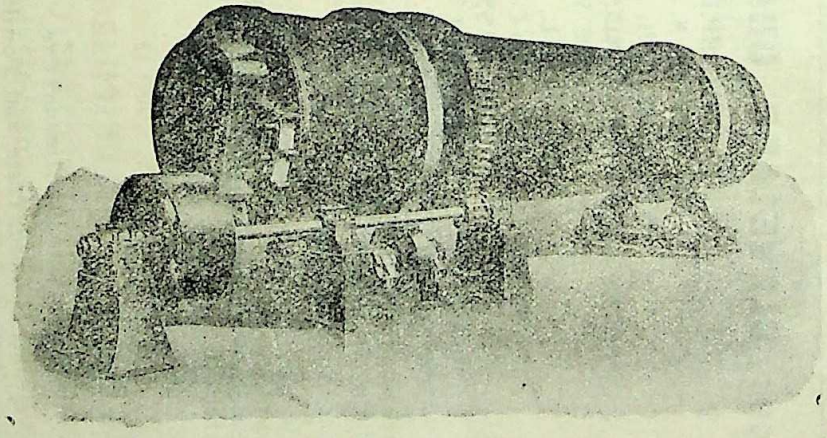
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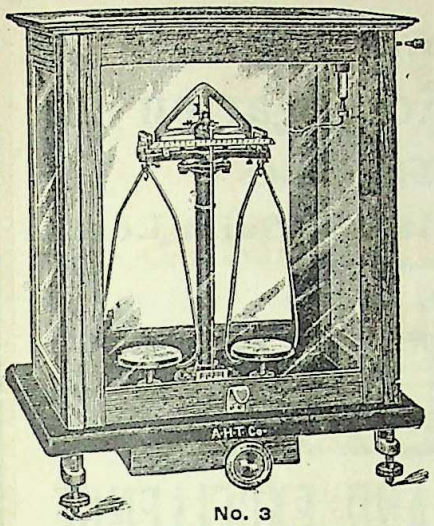
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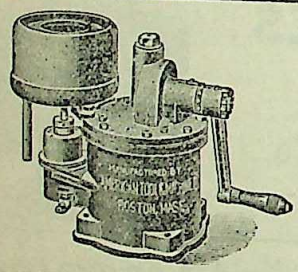
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Issued with the February Number, 1911.

Proceedings.

MINUTES OF THE FORTY-THIRD GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The forty-third general meeting of the American Chemical Society was held in the Chemical Building of the University of Minnesota, at Minneapolis, Minn., in affiliation with the American Association for the Advancement of Science, from Wednesday, December 28, to Saturday, December 31, 1910.

The meeting opened on Wednesday morning in general session and continued throughout the day, the following papers being presented:

Report for the International Committee on Atomic Weights, F. W. Clarke.
The Lost Arts of Chemistry. W. D. Richardson.
The Basis of Industrial Efficiency. Arthur D. Little.
Synthetic Metals from Non-metallic Elements. Herbert N. McCoy.
Progress in Food Chemistry. H. E. Barnard.
Mechanism of Cell Activity. Carl L. Alsberg.
Waste Wood and Some of Its By-Products. Geo. B. Frankforter.
Address by President McPherson, Section C, American Association for the Advancement of Science. Title: "The Formation of Carbohydrates in the Vegetable Kingdom."

Owing to the lack of time the address of Charles F. Burgess, which was to have been read in general session, was postponed until the following morning before the Section of Chemical Education.

The address of the retiring president, Wilder D. Bancroft, entitled "A Universal Law," was presented in the evening and was followed by an unusually attractive "smoker," which was enjoyed by all present, and each member who attended was presented with an attractive souvenir.

Thursday morning was given up to meetings of Divisions, as appears in the abstracted minutes of these meetings which follow this general report. The Section of Chemical Education also held a session on Thursday morning, which was largely attended and evoked much discussion. A program was arranged especially bearing upon the question of the education of industrial chemists and no meetings of the various industrial divisions were held in order that their members might be present.

Thursday afternoon excursions were held to the Minneapolis Flour Mills, St. Anthony Falls Water Power Plant, International Stock Food Plant and the Cream of Wheat Company.

On Friday morning the meeting was called to order in general session in the lecture room of the Chemistry Building of the University of Minnesota. The reports of the officers of the Society were read with the exception of the report of the editor of the *Journal of Industrial and Engi-*

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neering Chemistry, which had not been received, and the following miscellaneous business was transacted.

The President first announced the election of Alexander Smith as President of the Society and Louis Kahlenberg, F. K. Cameron, G. B. Frankforter and E. C. Franklin as Councilors-at-Large; also the election of E. G. Love as Councilor-at-Large to fill the unexpired term of Alexander Smith, made vacant by his election to the presidency. The President also announced the officers of the Society elected by the Council, which will be found in the Council minutes.

Dr. W. A. Noyes then presented an obituary notice prepared by Dr. Ira Remsen on the death of Professor Dr. Rudolph Fittig, our deceased honorary member.

A communication having been received in regard to the difficulties which chemists have in obtaining a proper denatured alcohol for laboratory use, the following resolution was presented:

WHEREAS, Under the present administration of the Denatured Alcohol Act, no suitable formula is permitted which gives the chemists of this country a product similar to the methylated alcohol so largely employed in analytical laboratories abroad, it is hereby moved that a committee be appointed to take up the question with the proper authorities and endeavor to obtain a denatured alcohol which will be available for laboratory use. DAVID WESSON.

President Bancroft appointed David Wesson, C. A. Crampton and Geo. P. Adamson a committee of three to carry this resolution into effect.

A unanimous vote of thanks was then passed to the President and Board of Regents of the University of Minnesota and the chemical faculty of that institution; to G. B. Frankforter, H. Snyder, F. C. Frary, C. F. Sidener, E. P. Harding, E. E. Nicholson and W. H. Hunter, chairmen of the local committees, and to the members of their committees, for their unceasing efforts in our behalf; also to Mrs. G. B. Frankforter and ladies of the faculty of the University of Minnesota; to the Commercial Club; to the business men of the city of Minneapolis, who had assisted in the entertainment of the Society, and to the following firms: Russell-Miller Milling Co., Pillsbury Flour Mills Co., Washburn-Crosby Co., Consolidated Milling Co., Minnesota Linseed Oil and Paint Co., Archer-Daniels Co., Midland Linseed Oil Co., St. Anthony Falls Water Power Co., Cream of Wheat Co., and International Stock Food Co.

The meeting then adjourned to meet in Divisions.

On Saturday afternoon the Society again enjoyed excursions to various manufacturing plants in Minneapolis and a sight-seeing trip through the "Twin Cities."

The meeting was enthusiastic throughout and 275 members and guests were present.

The papers read before the meeting will be found under the divisional heads which follow later.

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Report of the Secretary for 1910.

During the past year the American Chemical Society has sustained its rapid rate of growth, and the chemists of the country are thoroughly organized in hearty accord and sympathy with the work that their society is doing.

The publications are being received with interest at home and abroad, and through their influence American chemical research is being recognized the world over as rapidly approaching an equality with that of any other country.

The organization of the Society into Divisions has proved one of its wisest moves and their work is carried on with full enthusiasm by all of their members. Committees of the utmost importance are engaged on practical problems, as has been announced in the Proceedings from time to time, and the result of their work is sure to be of the highest importance.

The Boston meeting was the largest ever held in the history of the Society, and the San Francisco meeting, although at so great a distance from the chemical center of the country, was largely attended, and to the surprise of all was as large in attendance as any meeting ever held by the Society in the summer time. The incidents of the trip to California, the delightful hospitality of the California Section and the general interest and enthusiasm of the meeting will be a life-long memory for those who were so fortunate as to attend.

During the year the Society has again largely increased in membership and maintains, by an increased lead, its position as the largest chemical society in the world. The policy adopted a year ago of admitting corporation members into the Society on payment of yearly dues of twenty-five dollars has proved a wise move, for forty-two of the most prominent chemical corporations in the country have joined the Society and are contributing to its work and actively interested in its welfare. The Secretary wishes particularly to acknowledge the assistance of Mr. F. E. Gallagher, Secretary of the Industrial Division, and of Mr. B. T. Babbitt Hyde, in interesting several of these corporations and procuring them as members of the Society. The membership of the Society at the time of the Boston meeting was 4502. It is now 5081, a net gain of over 550 members. The membership statistics are as follows:

Honorary members	16
Life members	12
Corporation members	42
Members	5011
Total	5081
Elected during 1910 but not yet qualified	70
Grand total	5151

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During the year the Society has lost by death two of its honorary members, Stanislao Cannizzaro, of Rome, Italy, and Rudolph Fittig, of Strassburg, Germany; one of its life members, Charles B. Dudley, of Altoona, Pa.; and the death of the following members has been reported to the Secretary: George F. Barker, Philadelphia, Pa.; Clarence W. Beaver, San Francisco, Calif.; Constantin Fahlberg, Nassau a/d. Lahn, Germany; E. P. Coleman, Buffalo, N. Y.; Robert A. Duncan, Honolulu, Hawaii; F. A. Genth, Jr., Philadelphia, Pa.; Chas. A. Goessmann, Amherst, Mass.; Ottokar Hofmann, Kansas City, Mo.; H. W. Jayne, Philadelphia, Pa.; M. T. Jones, Jr., East Orange, N. J.; Albert E. Leach, Denver, Colo.; Horatio Loomis, New York City; Franklin C. Robinson, Brunswick, Me.; H. F. Rolker, Baltimore, Md.; Wm. H. Seaman, Washington, D. C.; August Seher, Newark, N. J.; W. A. Syme, Raleigh, N. C.; Henry A. Torrey, Cambridge, Mass.; Harold R. Wade, Washington, D. C.

The number of members not in arrears registered in the Local Sections on December 1, 1909, was 3237; the number on December 1, 1910, was 3667. The number in each Section for 1909 will be found in the Proceedings for 1910, page 13. For 1910 they are as noted below.

During the year the Local Sections as a whole have, as heretofore, shown strong loyalty to the welfare of the whole Society as against any special local interest and have met the spirit which pervades almost all of the Sections to exert due economy in their local expense in order that the funds of the Society may be utilized to meet the great cost of our publications. Most of the members realize fully that it is only by an income of at least ten dollars per member that the Society can continue to issue its present publications and increase their usefulness in proportion to the growth of the Society. Therefore every member secures the benefit of any sacrifice he may make in his own Local Section by the increased good which results to him and to the whole Society through its publications and through its divisional work.

The accounts of the Local Sections placed in the hands of the Secretary, to whom their treasurers make report, are as follows: The table gives a summary of the sectional accounts for the year, shows the number of members in each, the balance of funds retained by them from 1909 account and credited to their 1910 account and also the cash drawn from the Treasurer's office for 1910 expenses. The last column also brings forth clearly the cost of administration per member in each Section. It will be noted that the cost per member is not at all proportional to the size of the Section, some of the smallest Sections having the lowest expense account, while some of the larger have a greater cost per member. This does not of necessity mean any lack of due economy in sectional affairs, but may be due to local conditions such as inability to obtain a

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Chicago	255	00.00	150.00	0.59
Cincinnati	79	7.50[1]	125.00	1.50
Cleveland	120	10.23	60.23	0.50
Columbus	50	00.00	50.00	1.00
Cornell	45	00.00	50.00	1.11
Eastern New York	53	00.00	50.00	0.94
Georgia	35	6.65	31.65	0.90
Indiana	76	12.05	52.05	0.68
Iowa	46	00.00	69.00	1.50
Kansas City	91	20.50	120.50	1.32
Lehigh Valley	41	25.83	25.83	0.63
Louisiana	33	00.00	00.00	0.00
Louisville	27	10.20	10.20	0.38
Michigan	111	52.75	52.75	0.48
Milwaukee	46	00.00	50.00	1.09
Minnesota	67	4.86	54.86	0.82
Nebraska	24	4.61	34.61	1.44
New York	735	00.00	300.00	0.41
North Carolina	26	0.65	35.65	1.37
Northeastern	458	84.16	334.16	0.73
Philadelphia	235	00.00	150.00	0.64
Pittsburg	170	51.06	151.06	0.89
Puget Sound	31	00.00	42.50	1.37
Rhode Island	48	00.00	50.00	1.04
St. Louis	60	20.00	80.00	1.33
Syracuse	73	00.00	50.00	0.68
Univ. of Illinois	50	2.56	42.56	0.85
Univ. of Missouri	19	7.85	7.85	0.41
Washington	258	11.39	101.39	0.39
Western New York	66	28.26	98.26	1.49
Wisconsin	68	00.00	25.00	0.37
	3667	404.71	2598.71	0.71

During the fiscal year, December 1, 1909, to December 1, 1910, the Secretary has made collections to the amount of $54,507.06, divided as follows:

Members' dues and subscriptions	$47,112.00
Subscriptions from non-members	3,436.14
Sales of back numbers	2,641.98
Foreign postage	683.06
Reprints	338.43
Reinstatements	17.00
Exchange	12.14
Interest	266.30
	$54,507.06

[1] Cash returned to Treasurer.

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This amount was duly transmitted to the Treasurer of the Society.

The amount of sales of back numbers has kept up during the year far beyond the expectation of the Secretary and the income has been obtained largely through extensive advertising at home and abroad and by the increased estimation in which the Society's publications are held; also sales of full sets of the *Journal of the American Chemical Society* and of *Chemical Abstracts* have been much larger than in any previous year. In spite of this fact, by purchase of single back numbers and by reprinting at a low cost one or two of the smaller numbers in earlier volumes, the stock as a whole is in better condition than at the beginning of the year. The new storage house in the basement of the office of the Eschenbach Printing Company has proved entirely satisfactory and adequate for present needs; also it is convenient for the tri-monthly mailing of back numbers of the journals.

The following is a summary of the back numbers sent out by the Secretary during the year together with the present stock of journals and the condition of the mailing lists:

Copies of the Society's publications sent out from December 1, 1909, to December 1, 1910, aside from the mailing lists	26,499
Copies of the Journals and Chemical Abstracts in stock	49,048
Copies of the General Index in stock	477
Copies of the Anniversary Number in stock	293
Mailing list for both Journals and Abstracts	5,099
Mailing list for Abstracts only	167
Mailing list for Journal only	419
Mailing list for Industrial Journal only	152

The Secretary hopes that the members of the Society will carefully examine their back files for copies necessary to fill out sets which are regularly advertised for in the pages of the JOURNAL. Older members of the Society are especially requested to search for possible copies of Vol. 17, Nos. 1, 8 and 10; Vol. 18, Nos. 5 and 6; Vol. 20, Nos. 3 and 4; Vol. 22, No. 3.

The work of the secretarial office has greatly increased, owing to the increased numbers of the Society and the corresponding increase in the mailing lists, changes of address, collection of subscriptions and dues and bookkeeping incident thereto. It has, accordingly, become necessary to engage a third stenographer for three or four months of the year.

Owing to the rulings of the Post-Office Department in regard to societies issuing publications to their members as a part of their membership dues, an unusual amount of work has been necessary in order to try and pass remedial legislation through Congress. The Dodds Bill, presented to the House in the latter part of 1909, will give this relief to scientific societies and every possible effort has been put forth by the Secretary and by

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many members of the Society helping him in the work to secure its passage. The House Commitee at first opposed, later reported the bill unanimously, and it passed the House previous to the close of the last session.

Many of the other scientific societies of the country had, however, taken no interest in the matter, as the Post-Office Department was following the policy of attacking them one at a time, and the Secretary has been engaged since early summer time in a campaign of education and has organized a committee, of which Dr. H. W. Wiley is the active and efficient chairman, representing the majority of the prominent scientific and educational societies of the country. This committee is actively at work in Washington endeavoring to present our case to the Postmaster-General and the Senate Committee in order that the great injustice of the ruling and its certain adverse effects may be averted.

The Secretary wishes, at the close of his fourth term of office, to thank the members throughout the Society for their continued loyal support which they have given him in his efforts to increase the strength and usefulness of our Society for the upbuilding of American chemistry and he wishes to acknowledge the fact that without this help his efforts would count for little.

CHARLES L. PARSONS,
Secretary.

Report of the Editor of the Journal of the American Chemical Society.

During the year ending November 30, 1910, 225 papers have been submitted to the Board of Editors of the *Journal of the American Chemical Society*. Of these 195 have been published, 7 have been published after revision by the authors, 5 have been referred to the Editor of the *Journal of Industrial and Engineering Chemistry*, and 18 have been returned for revision or because they were not suitable for publication in the JOURNAL. The number of pages published during the past four years have been as follows:

	1907.	1908.	1909.	1910.
Proceedings.....	92	130	116	132
Original papers.....	1624	1736	1271	1492
Reviews.....	73	110	64	137
Book reviews.....	73	77	31	71

The circulation of the Journal for December, 1910, was 5099. The edition for January, 1911, will be 6100 copies. This is a very much larger circulation than that of any similar publication which is issued in the world. More than 400 copies of our Journal now go to foreign countries, and it has long been true that no other medium of publication than the Society's journals reaches more than a very small fraction of the members of the American Chemical Society. W. A. NOYES.

Report of the Editor of Chemical Abstracts for the Year 1910.

During the year just closing *Chemical Abstracts* has grown steadily, as will be seen from the various figures given below. In order to com-

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ply more conveniently with the postal regulations and to hasten the appearance of the annual index, the latter will this year take the place of the regular number 24, instead of being issued as an extra number as formerly. In spite of the holding over of material to 1911 which this involved, the 1910 volume contains nearly 300 pages more of abstracts than the 1909 volume, the total number of abstracts (exclusive of patents) being 13,006 as compared with 11,455 for 1909. The number of abstractors at the beginning of the year was 230; number at present, 253. With the June 20th issue was published a rewritten edition of Directions for Abstractors, and accompanying this a list of Periodicals Abstracted, with full information as to publisher, subscription price, etc. This list contained 435 periodicals; 8 have since been removed, owing either to discontinuance of publication or their poor returns for abstracting, and 59 new ones added, making a present total of 486. At the beginning of the year a new department of Immunochemistry was introduced. It is of interest to note that by condensation wherever practicable and the use of abbreviations the average length of an abstract has gradually been reduced, being 0.328 page in 1907, 0.283 in 1908, 0.233 in 1909 and 0.225 in 1910.

Statistics for the separate departments follow:

	No. of pages.	No. of abstracts.
Apparatus	47.3	301
General and Physical Chemistry	298.8	1229
Radioactivity	50.7	212
Electrochemistry	73.4	377
Photography	31.0	212
Inorganic Chemistry	103.4	409
Analytical Chemistry	102.2	446
Mineralogical and Geological Chemistry	68.2	417
Metallurgy	126.4	588
Organic Chemistry	632.0	1675
Biological Chemistry	331.1	1892
Immunochemistry	59.7	300
Foods	116.3	605
Nutrition	89.5	449
Water, Sewage and Sanitation	58.9	247
Soils and Fertilizers	76.3	505
Liquors	45.1	230
Pharmaceutical Chemistry	78.0	481
Acids, Alkalies, Salts and Sundries	39.0	228
Glass and Ceramics	32.4	180
Cement, Mortar, Etc.	50.9	216
Fuels	60.5	255
Petroleum, Asphalt, Etc.	43.3	185
Cellulose and Paper	17.0	83
Explosives	64.3	300
Dyes and Textil Chemistry	39.7	212
Pigments, Resins, Etc.	30.9	138

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	No. of pages.	No. of abstracts.
Fats, Fatty Oils and Soaps	37.5	178
Sugar, Starch and Gums	82.0	431
Leather and Glue	9.1	25
Patents	387.0	3754[1]
	3281.9	13006
Headings and Blanks	32.1	
	3314.0	

AUSTIN M. PATTERSON, *Editor.*

Treasurer's Report.

RECEIPTS.

Balance on hand December 1, 1909		$ 4,699.99
Secretary's office	$54,507.06	
Advertising	4,170.96	
Abstractors	2.33	
		58,680.35
Rebates on postage		1,990.61
Interest on bank balances:		
Farmers Loan & Trust Company	$ 354.12	
Knickerbocker Trust Company	45.44	
		399.56
Interest on investments:		
Atlas Portland Cement Bonds		120.00
Interest on special funds:		
Special investment fund	$ 70.00	
Life membership fund	103.18	
		173.18
Cash retained by Local Sections		397.21
		$66,460.90

December 1, 1909–November 30, 1910.

DISBURSEMENTS.

Journal:		
Editor's salary	$ 970.79	
Expenses	114.40	
Reviews	37.00	
Printing	7,326.20	
Author's reprints (gross)	619.44	
		$ 9,067.83
Chemical Abstracts:		
Editor's salary	$ 1,000.00	
Assoc. Editor's salary	866.66	
Assistance	1,646.81	
Abstractors	4,997.69	
Expenses	324.57	
Printing, including index	15,886.76	
		24,722.49

[1] Not included in the total.

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Journal of Industrial and Engineering Chemistry:		
Editor's salary	$ 916.63	
Clerical	560.00	
Expense	222.70	
Special expense	40.00	
Printing	4,978.76	
Authors' reprints (gross)	577.25	
		7,295.35
Commissions:		
Advertising	$ 271.45	
Collections	2,180.28	
		2,451.73
Secretary's office:		
Clerical	$ 1,198.41	
Expense	1,399.98	
		2,598.39
Treasurer's office:		
Salary	$ 200.00	
Expense	400.00	
		600.00
Librarian's office		500.00
General meetings		975.95
Local Sections		2,591.21
Incidentals		444.15
Back numbers		931.63
Directory		304.91
Investments of balance		10,521.24
Balance on hand at Farmers' Loan & Trust Co		3,456.02
		$66,460.90

December 1, 1910.

ASSETS.

Special investment fund:		
($2,000 3½ per cent. N. Y. C. gold bonds due 1915)	$ 2,097.50	
($10,000 U. S. Steel Corp. gold bonds (1963)	10,418.06	
		$12,515.56
Atlas Portland Cement Co. bonds, 6 per cent		2,210.00
Life membership fund:		
($1,000 3½ per cent. N. Y. C. gold bonds, due 1928)	$ 1,080.38	
In Emigrant Savings Bank	1,800.43	
		2,880.81
Balance:		
Cash on hand Farmers' Loan & Trust Co		3,456.02
Cash retained by Local Sections		397.21
		$21,459.60

LIABILITIES.

Life membership fund	$ 1,800.43	
Excess assets over liabilities	19,659.17	
		$21,459.60

A. P. HALLOCK, *Treasurer.*

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Report of the Finance Committee for 1910.

December 24, 1910.

To the Members of the American Chemical Society:

In accordance with the requirements of the Constitution of the Society your Finance Committee has audited and approved all bills paid by the Treasurer during the past year.

Acting under the authority of the committee, Messrs. J. Yalden & Co., certified public accountants, have audited the accounts of the Treasurer and have certified the same to be correct.

Respectfully submitted,

E. G. LOVE,
GEO. C. STONE,
PARKER C. MCILHINEY,
Finance Committee.

Report of the Librarian for the Year ending November 30, 1910.

EXPENSES OF THE LIBRARIAN'S OFFICE.

D. D. Berolzheimer, Librarian, in account with the American Chemical Society.

Dr.

To balance, Dec. 23, 1909, Dr. E. G. Love	$ 13.23	
To Treasurer, Dr. A. P. Hallock	500.00	
		$513.23

Cr.

By binding and completing files	$285.55	
By clerical services	72.00	
By salary	100.00	
By postage	4.53	
By incidentals	38.33	
		500.42
Balance Dec. 1, 1910		$ 12.82

Respectfully submitted,

D. D. BEROLZHEIMER, *Librarian.*

Division of Industrial Chemists and Chemical Engineers.

The meetings of the Division were held on Friday and Saturday with Chairman A. D. Little presiding.

The editor of the *Journal of Industrial and Engineering Chemistry* announced that the full proceedings with papers will be printed in the February number of his journal.

A special feature of the meeting was the Efficiency Symposium held on Friday morning.

Reports of progress were presented by the Committee on Standard Specifications and on Definition of Industrial Terms. A committee was also appointed to consider the question of improving the quality of platinum laboratory utensils.

It was voted to lay an assessment of one dollar per member upon the membership of the Division for carrying on divisional work.

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In the temporary absence of the chairman, Mr. William Brady, Chairman *pro tem.*, upon motion, appointed a committee consisting of W. D. Richardson, S. W. Parr and John White, to draft suitable resolutions expressing the appreciation of the Division for the work which its first chairman, A. D. Little, has accomplished in organizing and building up the Division of Industrial Chemists and Chemical Engineers.

The following officers were elected for the year 1911: *Chairman*, G. C. Stone, 55 Wall St., New York City; *Vice-Chairman*, William Brady; *Secretary*, F. E. Gallagher, 93 Broad St., Boston, Mass.; *Executive Committee*, Officers and Editor of the *Jouurnal of Industrial and Engineering Chemistry*, *ex-officio*, and H. S. Miner, J. O. Handy, W. H. Walker, Clifford Richardson, G. E. Barton.

JOHN WHITE, *Secretary pro tem.*

Division of Physical and Inorganic Chemistry.

The Division met on Thursday, Friday and Saturday, presided over by Vice-Chairman Alexander Smith.

The committee appointed to consider the advisability of separating the Division into a Division of Physical and a Division of Inorganic Chemistry submitted the following report, which was read and adopted.

REPORT OF COMMITTEE.

The committee, which consists of Drs. W. F. Hillebrand, T. W. Richards, Alexander Smith, H. L. Wells, and the undersigned, has reached the conclusion, by a vote of four to one, that it would be both unwise and undesirable to separate at the present time the Division of Physical and Inorganic Chemistry into a Division of Physical Chemistry and a Division of Inorganic Chemistry.

The chief reason for this conclusion lies in the very intimate relationship that exists between the two fields of work and in the difficulty that would be experienced in attempting to draw a line between physical and inorganic investigations, or between physical and inorganic investigators.

The discussion of this question was originally brought up in the hope of providing some relief from the inconvenience resulting from the great length of the programs of the Division. At the Boston meeting the program was so long that certain papers were slighted, and that many members were obliged to leave before the protracted meetings of the Division had come to an end. In view of these facts, the committee would recommend that measures be taken to remedy this difficulty in the future, and would make the following tentative suggestions:

First, that the time allotted to each paper be reduced to a minimum, and that the time limit be in each case strictly enforced by the chairman.

Second, that in case the program be unusually long, the papers be grouped (prior to the printing of the program) in two *temporary subdivisions*, of Physical and Inorganic Chemistry, respectively, care being

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taken whenever possible to avoid the simultaneous presentation of papers that are of unusually broad, general interest.

Respectfully yours,

A. W. BROWNE, *Chairman.*

It was voted that a committee consisting of the chairman and one other member appointed by him report at the Indianapolis meeting upon the two following questions:

First, the best means of raising from twenty to twenty-five dollars yearly for postage and printing, at present paid for by the Secretary.

Second, the desirability of an addition to the by-laws covering the eligibility of officers to re-election.

The Nominating Committee, consisting of H. L. Wells, E. W. Morley and H. N. McCoy, presented the following nominations and these officers were elected for the year 1911: *Chairman*, H. P. Talbot, Mass. Inst. Technology, Boston, Mass.; *Vice-Chairman*, W. Lash Miller; *Secretary*, S. L. Bigelow, Univ. of Michigan, Ann Arbor, Mich.; *Executive Committee*, Officers *ex-officio*, and W. D. Bancroft, W. F. Hillebrand, G. A. Hulett, T. W. Richards, R. B. Moore.

Of the following papers presented to the Division 29 were read and 19 presented by title only:

Direct Currents in a Closed Liquid Circuit. F. C. Frary and J. B. Bolton.

Electrical Equipment for Electroanalysis and Electric Furnace Work. F. C. Frary.

The Fluorescence of Anthracene. Wilder D. Bancroft.

Chemical Properties of Certain Radioactive Substances. B. B. Boltwood.

Equilibrium in Carbonate Solutions. Herbert N. McCoy.

Radioactivity of Thorium Products. Herbert N. McCoy.

Is the Action of the Enzyme Invertase Reversible? C. S. Hudson and H. S. Paine.

The Nature of Mass. J. E. Mills.

On the Mechanism of the Reactions of Alkyl Halides with Sodium Ethylate and with Sodium Phenolate. S. F. Acree, H. C. Robertson and E. K. Marshall.

The Effect of Certain Neutral Salts on the Hydrolysis of Ethyl Acetate at 100°. W. E. Henderson and D. R. Kellogg.

The Violet Coloration of Ferric Alums and Nitrate. W. E. Henderson.

The Function of the Walls in Capillary Phenomena. S. L. Bigelow and F. W. Hunter.

The Vapor Pressure of Dried Calomel. Alexander Smith and A. W. C. Menzies.

The Vapor Pressures of Sulfur. Alan W. C. Menzies.

A Lower Limit for the Critical Temperature of Mercury. Alan W. C. Menzies.

The Diffusion of Oxygen through Solids. G. B. Frankforter and R. S. Callaway.

Snow, as a Means of Studying the Smoke Nuisance. G. B. Frankforter.

Physical Properties of Aqueous Solutions Containing Ammonia and Citric Acid. Robert A. Hall and James M. Bell.

The Action of Hydrogen Sulfide on Certain Metallic Salts in Non-aqueous Solvents. W. G. Wilcox.

The Heat of Neutralization of Pyridine in Various Solvents. J. Howard Mathews.

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The Use of a Dewar Flask in Measurements of Heats of Neutralization. J. Howard Mathews and A. F. O. Germann.

Surface Tension Measurements at the Surface between Two Liquids. W. D. Harkins.

Equilibrium in the System Lead Nitrate, Pyridine. J. H. Walton, Jr., and R. C. Judd.

The Action of Oxides of Lead on Normal Potassium Tartrate. F. C. Krauskopf.

On the Interaction of Metallic Sodium and Mercury. L. Kahlenberg and David Klein.

A New Hydrogen Sulfide Generator. J. I. D. Hinds.

Sulfite Method for Separating Strontium and Calcium. J. I. D. Hinds.

Electric Osmose. Harry N. Holmes.

The Rapid Determination of Silver and Cadmium by Means of the Gauze Cathode and Stationary Anode. R. C. Benner and W. H. Ross.

The Rapid Deposition of Cobalt and Nickel by Means of Gauze Cathode and Stationary Anode. R. C. Benner and W. H. Ross.

The Effect of Continued Grinding on Water of Crystallization. Nicholas Knight.

Nucleation of Mixed Vapors in Dust-free Air. I. H. Derby and E. X. Anderson.

Apparatus for Measuring Vapor Pressure. I. H. Derby, F. C. Gutsche and F. Daniels.

The Tendency of Chemical Energy Conversion. J. E. Siebel.

The Determination of Manganese by the Sodium Bismuthate Method. M. H. P. Brinton.

The Sulfur Hydrosol Prepared by a New Method. Harrison Everett Ashley.

Recrystallization of Barium Sulfate. H. C. Cooper and T. S. Fuller.

The Dielectric Capacity of Some Liquid Hydrides. R. C. Palmer and Herman Schlundt.

A Case of Ammonia Deliquescence. W. P. Bradley.

The Action of Ammonia upon Ammonium Sulfocyanide. W. P. Bradley.

On the Electrochemical Oxidation of Hydrazine. J. W. Turrentine and Willis A. Gibbons.

Contribution to the Electrochemistry of Hydronitric Acid: the Electrochemical Corrosion of Some Metals in Sodium Trinitride Solution. J. W. Turrentine.

Experiments on the Reliability of the Borax Bead Test for Varying Mixtures of Nickel and Cobalt. P. Rothberg and L. J. Curtman.

A Study of the Factors Influencing the Systematic Qualitative Determination of Barium. E. Frankel and L. J. Curtman.

A New Indicator. Chas. P. Fox.

Rapid Electrolytic Deposition of Metals from Boiling Solutions. Franz F. Exner.

The Pocket Spectroscope—A Neglected Necessity for the Practical Chemist. Chas. S. Palmer.

The Solubility of Salts in Solutions of Salts of Various Types. W. D. Harkins. "Carnegie Publication."

S. L. BIGELOW, *Secretary.*

Division of Fertilizer Chemistry.

The meeting of the Fertilizer Division was held on Friday, December 30th, and was presided over by Chairman F. B. Carpenter.

The Editor of the *Journal of Industrial and Engineering Chemistry* has announced that the full proceedings will appear in his February journal.

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The following officers were elected for the year 1911: *Chairman*, P. Rudnick, cr. Armour & Co., Union Stock Yards, Chicago, Ill.; *Vice-Chairman*, J. P. Street; *Secretary*, J. E. Breckenridge, Carteret, N. J.; *Executive Committee*, Officers *ex-officio*, and F. B. Carpenter, A. Lowenstein, W. J. Jones, Jr., G. Farnham.

Reports of the committees on Phosphoric Acid, Potash, Nitrogen, and Legislation were received and accepted.

The chairman's address, entitled "Results of Soil Investigations as Affecting the Use of Fertilizers," was read before the Division.

J. E. BRECKENRIDGE, *Secretary*.

Division of Agricultural and Food Chemistry.

The Division met on Friday, December 30th, presided over by Chairman H. E. Barnard.

The officers elected for the year 1911 are: *Chairman*, H. E. Barnard, State Laboratory of Hygiene, Indianapolis, Ind.; *Vice-Chairman*, A. L. Winton; *Secretary and Treasurer*, B. E. Curry, Durham, N. H.; *Executive Committee*, Officers *ex-officio* and H. W. Wiley, J. P. Street, G. F. Mason.

Details of the meeting with a list of papers presented have been announced for the February issue of the *Journal of Industrial and Engineering Chemistry* and will not be repeated here.

B. E. CURRY, *Secretary*.

Division of Organic Chemistry.

The Division met on Thursday, December 29th, and was presided over by G. B. Frankforter, as the chairman was unable to be present. W. J. Hale was elected Secretary *pro tem*.

It was voted that memorial resolutions in honor of Professor H. A. Torrey should be placed on file in the minutes of the Division and a copy sent to Mrs. Torrey.

It was voted that an assessment of one dollar be levied upon each member of the Division to defray present indebtedness ($14.67) and to provide for future expenditure.

The following officers were elected for 1911: *Chairman*, G. B. Frankforter, University of Minnesota, Minneapolis, Minn.; *Secretary*, Wm. J. Hale, University of Michigan, Ann Arbor, Mich.; *Executive Committee*, Officers *ex-officio*, and M. T. Bogert, C. S. Hudson, Wm. L. Evans.

Of the following papers 10 were presented and 7 read by title only.

WM. J. HALE, *Secretary pro tem*.

Division of Pharmaceutical Chemistry.

The Division met on Thursday, December 29th, and was presided over by Chairman A. B. Stevens.

After the appointment of a Nominating Committee, consisting of Messrs.

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Kremers, Barnard and Newcomb, the address of the chairman upon "Pharmacopeial Standardization" was read.

The report of the Committee on Quantitative Methods was read and discussed and it was voted that B. L. Murray prepare the report for publication and submit it to various journals.

The following officers, on nomination from the committee, were then elected for 1911: *Chairman*, B. L. Murray, Rahway, N. J.; *Vice-Chairman*, A. D. Thorburn; *Secretary*, F. R. Eldred, 3323 Kenwood Ave., Indianapolis, Ind.; *Executive Committee*, Officers *ex-officio*, and A. B. Stevens, L. F. Kebler.

The following papers were then read:

Citro Compounds of Iron. A. B. Stevens.

Camphor in Oil of Sassafras. E. R. Miller and G. H. Marsh.

Assay of Gelsemium. L. E. Sayre.

Rapid Determination of Sulfuric Acid with the Porous Clay Crucible. F. Klein.

Chemical Problems Suggested by the Cultivation of Medicinal Plants. (1) Stramonium. E. Kremers.

B. L. MURRAY, *Retiring Secretary.*

Section of Chemical Education.

The Section of Chemical Education met on Thursday morning in joint session with the Division of In[illegible]ial Chemists and Chemical Engineers, the Division of Fertilizer Chem[illegible]nd the Division of Agricultural and Food Chemists. The meeting was presided over by Chairman C. F. Burgess, who presented an address entitled "The Efficiency of the College Graduate in the Chemical Industry." The address was thoroughly discussed and the following papers were then presented:

A Laboratory Course in Chemical Engineering. W. H. Walker and Wm. K. Lewis.

Points of View in Teaching Industrial Chemistry. J. R. Withrow.

The Acquirement of Proficiency in Qualitative Analysis. An Inquiry into American Teaching Methods. H. C. Cooper.

The Preparation of "Known" Solutions in Qualitative Analysis. L. J. Curtman.

Instruction in Physical Chemistry. Two Modifications. R. Stevenson.

Suggestions as to Certain Desirable Changes in Chemical Nomenclature. Edwin Booth.

Quantitative Analysis as a Science. W. D. Harkins.

The Use of the Blue Print. Francis C. Frary.

Section of Biological Chemistry.

The section met on Thursday, December 29th, and Friday, December 30th, under the chairmanship of C. L. Alsberg with the assistance of I. K. Phelps as secretary.

The program was unusually interesting and a large number of papers were presented, of which the following is a list:

The Iodine Content of a Physiologically Active Substance Obtained from the Large, Medium, Small and Mixed Thyroid Glands of Beef, Hogs and Sheep. T. B. Aldrich.

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Further Studies on the Growth of Plants in Bacterial Transformation Products. A. Dachnowski.

The Antitoxic Action of Certain Nutrient and Non-nutrient Mineral Bases with Respect to Plants. M. M. McCool.

The Relation of Certain Odorous Constituents of Plants to Plant Metabolism. Frank Rabak.

The Influence of Shade on Sugar Accumulation in Tobacco in the Tropics. H. H. Hasselbring.

The Chromogen of the Hawaiian Bitter Yam. H. H. Bartlett.

The Preparation and Properties of an Oxidase Occurring in Fruit. H. P. Bassett and Firman Thompson.

A Quantitative Method for the Estimation of Oxidases. H. H. Bunzel.

The Oxidative and Catalytic Power of Soils and Subsoils. M. X. Sullivan and F. R. Reid.

Enzymotic Activities of Soils. O. Schreiner and M. X. Sullivan.

The Organic Matter of Soils as Material for Biochemical Investigation. O. Schreiner and E. C. Shorey.

The Isolation of Creatinine from Soils. E. C. Shorey.

The Toxic Action of Organic Compounds as Modified by Fertilizer Salts. O. Schreiner and J. J. Skinner.

The Processing of Japanese Persimmons. H. C. Gore.

The Alkaloid Content of Ergot and its Fluid Extract. A. Seidell.

The Poisonous Properties of the Mushroom *Inocybe Infida*. E. D. Clark.

One Role of Carbonic Acid in Fermentation. C. S. Hudson.

Studies upon the Biochemistry of *Penicillium*. O. F. Black.

The Action of the Fungus *Diplodia* upon Some Phosphorous Compounds of Maize. A. S. Reed.

The Fermentation of Citric Acid in Milk. A. W. Bosworth and M. J. Prucha.

Studies in Thermal Death-points of Milk Enzymes. W. N. Berg.

On the Catalase Content of Tissues and Organs after Prolonged Fasting. P. B. Hawk.

The Lecithin Content of Milk under Pathological Conditions. L. W. Fetzer.

Studies on Lipoid Potassium Compounds of the Tissues. W. Koch and C. C. Todd.

"Normal" Arsenic in the Human Body. R. L. Emerson.

The Non-existence of So-called "Normal Arsenic" in the Human Thyroid Gland. Wm. H. Warren.

Demethylation in the Body. W. Salant and I. K. Phelps.

Some Experiments on the Influence of the Digestive Process on the Excretion of Carbon Dioxide. G. O. Higley.

The Incompatibility of Alcohol with Certain Nutrients. J. E. Siebel, Jr.

Nutrition Investigations, No. 30. Further Improvements in the Methods of Analyzing Flesh. A. D. Emmett and W. E. Joseph.

A Method for the Estimation of Reducing Sugars. S. R. Benedict.

On Luciferesceine, the Fluorescent Material Present in Certain Luminous Insects (Preliminary). F. Alex. McDermott.

A Note on Fat Synthesis in the Human Intestin. H. M. Adler.

On the Neutrality Equilibrium in Blood and Protoplasm. The Regulatory Activity of the Kidney. L. J. Henderson.

Chloroform Narcosis and Fatty Degeneration in the Hearts of Nephrectomized Rabbits. F. H. McCrudden (with Paul A. Lewis).

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A Study in the Exact Determination of Total Nitrogen in the Feces. I. K. Phelps.

Studies upon the Extractives of the Maize Embryo. C. L. Alsberg.

The Excretion of Chlorides under the Influence of Copious Water Drinking between Meals. S. A. Rulon and P. B. Hawk.

A Rapid Method for the Production of Immune Serd. J. P. Atkinson.

The Resorption of Fat. P. F. Trowbridge.

Plants which Require Sodium. W. F. V. Asterhout.

Inosinic Acid. P. A. Levene and W. A. Jacobs.

Yeast Nucleic Acid. P. A. Levene and W. A. Jacobs.

The Distribution of Nucleariddases in Animal Tissues. P. A. Levene and F. Medigrecean.

Certain Aspects of the Chemical Study of the *Monardas*. Edward Kremers.

All of the above minutes abstracted and edited from the originals, which are held on file.

CHARLES L. PARSONS,
Secretary, American Chemical Society.

COUNCIL.

The Council of the American Chemical Society met in the Chemical Building of the University of Minnesota at 4 P.M., Wednesday, December 28th, with the following Councilors present: E. P. Harding, Walter P. Schuck (substitute for H. G. Byers), Percy H. Walker, C. L. Alsberg (substitute for L. M. Tolman), C. S. Hudson (substitute for W. B. D. Penniman), B. T. Babbitt Hyde (substitute for Charles Baskerville), W. L. Dudley, E. G. Love, Geo. P. Adamson, H. E. Barnard, F. B. Carpenter, B. E. Curry (substitute for W. L. Jennings), E. W. Rockwood, F. K. Cameron, H. D. Batchelor (substitute for W. R. Clymer), S. W. Parr, W. D. Richardson, W. R. Smith, Geo. N. Prentiss, William Brady, Wm. McPherson, J. H. Long, H. P. Talbot, S. L. Bigelow, A. B. Stevens, John White, Edward Bartow, Austin M. Patterson, W. A. Noyes, T. J. Parker, G. B. Frankforter, H. N. McCoy (substitute for J. Stieglitz), Alexander Smith, A. D. Little.

It was voted that the exact date of the Indianapolis meeting should be left to the President and the Secretary with power.

It was voted that it is the sense of the Council that the American Chemical Society should assist in every possible way the officers of the Eighth International Congress of Applied Chemistry and that the Secretary and the Editor of the *Journal of Industrial and Engineering Chemistry* be respectively authorized to insert notices in the Proceedings of the Society and in the *Journal of Industrial and Engineering Chemistry* and to aid otherwise as occasion may warrant.

It was voted that the question of printing advertisements on the front covers of the journals of the Society be referred to a committee consisting of the three Editors of the Society with power.

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It was voted to refer the question of procuring a book plate for the library to the Librarian, President and Secretary, with power.

It was voted that all questions affecting the matter of advertisement in the journals of the Society and of their entrance or re-entrance to secure or continue the right to second-class postage be referred to the Directors, with power.

A petition having been received signed by twenty members in good standing for the formation of a Local Section in Nashville, Tenn., it was voted to authorize the formation of such a Section with a radius of fifty miles from Nashville in the State of Tennessee and extraterritorial rights for a period of five years only to the towns of Sewanee and Richard City.

A request having been received from the Washington Section for an extension of its territory to cover that portion of the State of Virginia recently surrendered to the Society, it was voted to lay the matter on the table until the Indianapolis meeting in order that the full question of territory, expenses and representation of Local Sections might be taken up by a committee and reported on at that meeting.

It was voted that the questions raised with regard to the Local Sections, especially with regard to the expenses of the Sections in relation to their membership and also with regard to representation in the Council, be referred to the Secretary and President-elect for consideration and recommendation at the Indianapolis meeting.

A duly signed petition having been received for the formation of a Local Section in Los Angeles, covering the territory of southern California, it was voted to grant the formation of such a Section with headquarters at Los Angeles and territory within a radius of seventy-five miles of that city provided a proper waiver of jurisdiction was obtained from the California Section.

It was voted that the question of publishing an Agricultural and Food Journal be laid on the table till the Indianapolis meeting and that the committee be requested to present a more detailed recommendation with regard to the publication of such a journal.

It was voted that the Secretary be requested to send out with the preliminary notices of the Indianapolis meeting a stamped postal card asking for subscriptions for a quinquennial index to *Chemical Abstracts* at $5.00 per volume.

It was voted that the Secretary be directed to write L. P. Kinnicutt and Wm. McMurtrie, expressing on behalf of the Council their sincere regret at their illness, their disappointment that they were unable to be present at Minneapolis, and their hearty good wishes for a speedy recovery.

It was voted that a committee of three be appointed to consider the advisability of forming a Division of Biological Chemists and to report

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their findings at the Indianapolis meeting. The President appointed C. L. Alsberg, Edward Kremers and P. A. Levene.

The meeting then adjourned.

A second meeting of the Council was called to order in the Dyckman Hotel at 8.30 P.M., Thursday, December 29th, with the following Councilors present: B. E. Curry (substitute for W. L. Jennings), Walter P. Schuck (substitute for H. G. Byers), Wm. McPherson, W. L. Dudley, S. W. Parr, Perry Barker (substitute for H. J. Skinner), C. L. Alsberg (substitute for L. M. Tolman), W. R. Smith, H. E. Barnard, E. W. Rockwood, F. K. Cameron, C. S. Hudson (substitute for W. B. D. Penniman), T. J. Parker, Austin M. Patterson, A. D. Little, H. D. Batchelor (substitute for W. R. Clymer), W. A. Noyes, H. P. Talbot, E. G. Love, Percy H. Walker, Geo. P. Adamson, Geo. B. Frankforter, B. T. Babbitt Hyde, Edward Bartow, F. B. Carpenter, John White, J. H. Long, W. D. Richardson, William Brady, Geo. N. Prentiss, H. N. McCoy (substitute for J. Stieglitz), E. P. Harding, S. L. Bigelow, Alexander Smith.

The Treasurer's report was read and accepted.

The following budget, after being considered section by section, was approved and recommended to the Directors for adoption:

ESTIMATED RECEIPTS 1911.

Membership dues and subscriptions	$47,500.00	
Advertisements	6,500.00	
Subscriptions, non-members	3,000.00	
Foreign postage	700.00	
Back numbers	1,000.00	
Interest	500.00	
		$59,200.00

ESTIMATED EXPENDITURES, 1911.

Journal American Chemical Society:		
Editor's salary	$ 1,000.00	
Expenses	200.00	
Reviews	100.00	
Printing	8,150.00	
Reprints (net)	350.00	
Chemical Abstracts:		
Salary, editor	1,200.00	
Salary, associate editor	1,100.00	
Assistance, including indexer	1,975.00	
Expenses	400.00	
Abstractors	7,150.00	
Printing, including index	17,954.00	
Journal Industrial and Engineering Chemistry:		
Salary, editor	1,000.00	
Expenses	300.00	
Printing, including index	6,240.00	
Clerical	720.00	
Special expense	300.00	

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Secretary's office:		
Clerical	1,500.00	
Expense	1,350.00	
Treasurer's office:		
Salary	250.00	
Expense	400.00	
President's office	50.00	
Librarian's office:		
Expense	400.00	
Salary	200.00	
Clerical	100.00	
General meetings	685.00	
Commission, advertisements at 20 per cent	1,300.00	
Commission, collections at five per cent	2,635.00	
Local Sections	2,500.00	
Incidentals	800.00	
Back numbers	600.00	
Printing adv. pages, J. I. E. C. (contingent expense)	800.00	
		$61,709.00

It was voted that the official colors of the Society should be gold and dark cobalt-blue.

It was voted that the Committee on Section of Chemical Education be continued and be given charge of a session of this Section for the Winter Meeting of 1911.

It was voted that the status of the Committee on Water Analysis be referred to the President-elect and the members of that committee with instructions to report at the Indianapolis meeting.

A communication having been received from I. K. Phelps in reference to the desirability of adopting some system for securing an endowment fund through bequests or otherwise, it was voted that a committee of three be appointed to consider the matter and report at the Indianapolis meeting. The President appointed B. T. Babbitt Hyde, M. T. Bogert and I. K. Phelps.

A report was received from the Chairman of the Supervisory Committee on Methods of Analysis, which was accepted and ordered printed.

To the Council of the American Chemical Society:

As Chairman of the Supervisory Committee on Methods of Analysis, I respectfully submit the following report:

The resolutions governing committees of this Society, and of its Divisions, having to do with the standardization of methods of analysis, which were adopted by the Council at the San Francisco meeting in July last, abolished the sub-committee on Phosphate Rock Analysis and transferred to the control of the Division of Industrial Chemists and Chemical Engineers the sub-committee on Soap and Soap Products. These and all other divisional committees having to do with methods of analysis, as well as the representatives of this Society on committees acting jointly with representatives of other societies, were placed under the control of the Supervisory Committee on Methods of Analysis in respect to their final reports, which are subject to approval by the Supervisory Committee before they can be published. The Supervisory Com-

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mittee is also charged with the duty of preventing useless overlapping of work by those committees.

The committees now in existence, their membership, and the problems under investigation are as follows:

I. JOINT COMMITTEES WITH OTHER SECTIONS.

1. Committee on Unification of Methods for the Analysis of Fats and Oils and their By-Products. Representing the American Chemical Society; A. H. Gill, *Chairman*, C. E. Waters, David Wesson, together with representatives of the Association of Official Agricultural Chemists and the American Society for Testing Materials.

I am informed by the Secretary of this Joint Committee, Mr. C. N. Forrest, that not much has been accomplished up to the present, but that preliminary work has been started looking toward the standardization of methods for the determination of specific gravity and for cold tests of fats and oils. It is the purpose of the committee to make a canvas of the methods now in use in this country in the oil and fat industry, and to carefully consider the matter of coöperation with committees abroad before any movement is made toward the formation of an International Commission. A report of progress was presented at the meeting last summer of the American Society for Testing Materials by the chairman of the committee representing that organization on the Joint Committee.

2. Committee on the Revision of Methods of Coal Sampling and Analysis. Representing the American Chemical Society, N. W. Lord, *Chairman*, Perry Barker, W. F. Hillebrand, A. H. White, together with representatives of the American Society for Testing Materials. The above-named representatives of the American Chemical Society have been designated by the Division of Industrial Chemists and Chemical Engineers to represent that Division also.

The committee as a whole does not seem to have been active during the past year and I have not as yet received from its chairman a statement of the present condition of its work.

II. DIVISIONAL COMMITTEES.

1. Division of Industrial Chemists and Chemical Engineers.

(*a*) Committee on Standard Methods of Technical Analysis, Andrew A. Blair, *Chairman*, Arthur M. Comey, J. O. Handy. This committee is not yet active. It remains for the Division to which it is subject to determin whether or not the committee named next below shall be subordinate to or coördinate with the above committee.

(*b*) Committee on Soap and Soap Products, W. D. Richardson, *Chairman*, Arthur M. Comey, R. E. Devine, S. E. Emery, B. T. B. Hyde, A. C. Langmuir, J. W. Loveland, Wilson H. Low, Ernest Twitchell, David Wesson. This committee was originally established as a sub-committee of the Committee on Uniformity in Technical Analysis (now Supervisory Committee on Methods of Analysis) to study the methods of analysis for soap and glycerin, with special reference to the soap industry. Its scope was soon widened, in 1908, to cover the fats and oils used in manufacturing soap, and special sub-committees were formed among its members to deal with special fields of investigation.

A special sub-committee on Glycerin, so I am informed by Mr. Richardson, is about ready to present a final report, after consultation abroad by certain of its members with corresponding English, French, and German committees, and at home with two representatives of the English Committee, who visited the country.

A special sub-committee on Fats and Fatty Oils is ready to publish tentative methods for the purpose of inviting criticism and suggestions. Coöperative work will be

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continued during the coming year and the hope is expressed that a final report can be made in a year's time.

There seems to be danger of an overlapping of the work of this special sub-committee with that of the Joint Committee on Unification of Methods for the Analysis of Fats and Oils and their By-Products, above referred to. I am informed, however, that the objects of the two committees differ to such an extent that no duplication of work has occurred.

It seems almost necessary to take up only one branch of work at a time, therefore other special sub-committees of committee (*b*) have not begun active work.

2., Division of Fertilizer Chemists.

(*a*) Committee on Potash Analysis, J. E. Breckenridge, *Chairman*, F. B. Porter, E. L. Baker. The work of this committee has been a comparison of methods as suggested by the chairman (*J. Ind. Eng. Chem.*, 1, 804). Some positive results seem to have been obtained.

(*b*) Committee on Phosphoric Acid Analysis (also Ammonium Citrate), G. A. Farnham, *Chairman*, W. J. Gascoyne, W. J. Jones, W. F. Hand, J. R. Powell. This committee has in hand the determination of insoluble phosphoric acid in fertilizers and also the preparation of ammonium citrate.

(*c*) Committee on Nitrogen Analysis, P. Rudnick, *Chairman*, C. H. Jones, F. C. Atkinson. At the time of the chairman's report to me, this committee was preparing its report on the coöperative work done last winter and spring. The nature of further work will be taken up, probably at the Minneapolis Meeting of the Society.

(*d*) Committee on Phosphate Rock Analysis, C. F. Hagedorn, *Chairman*, H. P. McConnell, W. D. Richardson, A. M. Peter, F. P. Veitch, S. W. Wiley. This committee is actively at work, but is not ready to report more than progress.

III. DIVISION OF PHARMACEUTICAL CHEMISTS.

Committee on Quantitative Methods, Frank O. Taylor, *Chairman*, Linwood A. Brown, B. L. Murray, L. D. Havenhill, A. P. Sy. The object of this committee, "as so far developed, is primarily to investigate methods of analysis which could be used for those chemical preparations of the United States Pharmacopeia which at the present time have definit purity requirements without any corresponding method of assay." As a beginning, the various mercuric salts are under investigation.

IV. SECTION OF INDIA RUBBER CHEMISTS.

Committee on Analysis of Rubber and Rubber Products, Chas. M. Knight, *Chairman*, Edward A. Barrier, Harvey M. Eddy, Wm. C. Geer, Chas. C. Goodrich, Wm. F. Hill, Frederic J. Maywald, Milton E. MacDonald, Geo. Oenslager, S. P. Thatcher. This committee has decided to limit its first work to the determination of total sulphur, free sulphur, and mineral matter in soft cured goods. It is expected that a preliminary report will be made to the Division of India Rubber Chemists during the Minneapolis meeting of the Society.

Respectfully submitted,

W. F. HILLEBRAND,

Chairman, Supervisory Committee on Methods of Analysis.

WASHINGTON, D. C., December 23, 1910.

The following report of the Committee on Museum was received, accepted and ordered printed:

Report of the Committee on Museum.

To the Council of the American Chemical Society:

The Committee on Museum has not been able to make very much progress, owing to the fact that the Chemists' Club has not yet entered into possession of its new quarters in New York City.

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According to our understanding, there will be available for museum purposes a well-lighted room about $23^1/_2$ feet wide and 14 feet high; this height will admit of a gallery over about one-half of the superficial area. It is the opinion of the committee that such space will be ample for many years to come, provided the collection is carefully restricted to materials and objects of real scientific and historic value. Mere personal memorabilia must, necessarily, be excluded, and doubtless the Chemists' Club would find free space in which to accommodate them.

Your committee is now formulating plans for the adoption of standard systems for the storage and cataloging of the chemicals and specimens which are to constitute the main collection of the Museum, and hopes to be able to report material progress at the time of the Summer meeting.

Respectfully submitted,

MORRIS LOEB,
VIRGIL COBLENTZ,
JACOB HASSLACHER,
RALPH MCKEE, *per* M. L.,
MOSES GOMBERG, *per* M. L.

NEW YORK, December 17, 1910.

The Committee on the Analysis of Fats and Oils reported as follows:

The Committee has held joint sessions with those of the A. O. A. C., and A. S. T. M. and is at present working upon the determination of the cold test and considering the question of temperature for specific gravity determinations. A more extended report will be furnished later.

Respectfully submitted,

A. H. GILL, *Chairman.*

It was voted that the report be accepted.

The election of the following officers by the Council and members at large was then announced: *President,* Alexander Smith; *Councilors,* Louis Kahlenberg, F. K. Cameron, G. B. Frankforter, E. C. Franklin.

A vacancy having been made by the election of Alexander Smith to the presidency, it was voted that E. G. Love, who stood fifth on the list of Councilors voted for by the membership, should be designated by the Council to fill the unexpired term.

The following officers were then elected for 1911: *Finance Committee,* E. G. Love, G. C. Stone, Arthur E. Hill; *Membership Committee,* Wm. McMurtrie, Chas. L. Parsons, B. E. Curry; *Directors,* Jan., 1911, to Jan., 1913, M. T. Bogert, T. J. Parker; *Secretary,* Chas. L. Parsons; *Treasurer,* A. P. Hallock; *Librarian,* D. D. Berolzheimer; *Editors, Journal of the American Chemical Society,* W. A. Noyes, Editor-in-Chief; M. T. Bogert, Edward Hart, W. F. Hillebrand, J. H. Long, Arthur A. Noyes, Chas. L. Parsons, H. P. Talbot, H. W. Wiley, Associate Editors. *Chemical Abstracts,* A. M. Patterson, Editor-in-Chief; J. J. Miller, Associate Editor.

At this point the committee appointed to consider the whole matter of *Industrial Journal* reported. After a lengthy discussion and one or two changes from the original draft, the following report was adopted by the Council:

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Report of Committee on Journal of Industrial and Engineering Chemistry.

The committee appointed by the President under authority of a special vote of the Council "to investigate the whole question of the *Industrial Journal* with reference to possible greater efficiency of that periodical," has taken up the delicate and difficult task assigned to it with full appreciation of the responsibilities involved and a very sincere desire to consider the whole question as fairly and impersonally as possible with sole reference to the best interests of the Society as the committee sees them.

In submitting this report, your committee feels that it can in no wise be regarded as presenting findings based upon a complete study of the many phases of the situation, nor did such a study seem possible, in view of the distance separating the members and the comparatively short time available. It is believed, nevertheless, that the broader aspects of the problem have been studied with a degree of thoroughness and care which justifies the findings and recommendations of the report.

The committee as appointed by the President is constituted as follows: A. D. Little, *Chairman*, T. J. Parker, Wm. Brady, W. C. Geer, W. R. Whitney, W. D. Bigelow, L. H. Baekeland.

The committee has held four meetings, at all of which the first four members named above were present. The views of Dr. Whitney, Dr. Baekeland and Dr. Bigelow were presented in writing, and carefully considered, and in addition thereto, the members of the committee present had the benefit of a further expression of Dr. Bigelow's opinions as entrusted by him to Mr. Walker, who appeared before the committee at one meeting. Individual members of the committee have discussed from time to time with officers of the Society many of the points under consideration; other questions have been referred to the printer. A series of specific inquiries has been sent out to one hundred of the more prominent members of the Society, selected for the most part from among the industrial chemists, and to these inquiries about fifty replies have been received and tabulated. A voluminous correspondence having to do with the business of the Journal has been reviewed. Dr. Love, of the Finance Committee, has appeared before the committee by request, and furnished certain desired information, and finally the committee has reviewed very fully and frankly all the points under consideration with the Editor of the *Industrial Journal*, at a special meeting, and desires particularly to express its appreciation of the spirit of friendly coöperation in which the Editor responded to the inquiries of the committee.

So far as can be determined from the replies received to specific inquiries, it would appear that a considerable proportion of our membership are well pleased, and some entirely satisfied with the *Industrial Journal* in its present form. A considerably larger proportion are for the most part emphatic in stating that the Journal does not meet their wants. From the general character of the two sets of replies, even more than from their numerical proportions, it would seem to your committee that the protests were entitled to the greater weight. They seemed for the most part to be based upon careful consideration and mature thought, whereas many of the other replies were distinctly casual in tone. When, however, the replies as a whole are studied for constructive criticism, specific objection and definite suggestion, such bewildering diversity of opinion is developed as to make it evident that no journal could possibly meet all requirements. It appears further that in the opinion of many members the present Journal is not true to name, and presents an undue proportion of food, agricultural and analytical papers to the practical exclusion of the desired papers dealing with chemical industry and chemical engineering.

Despite the discouraging diversity of opinion among the members of the Society as to what constitutes a thoroughly satisfactory and representative journal of industrial and engineering chemistry, your committee is emphatically of the opinion that

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the publication of such a journal by the Society is not only possible, but a duty which cannot be ignored or set aside. With the development in industrial chemistry which is assured in this country within the next few years, the constant increase in the number of industrial laboratories and chemists who devote themselves to industry, and the rapidly growing appreciation of the importance of the industrial branch of our science, your committee believes that it should be possible to develop here, under the auspices and direction of this Society, the best journal of applied chemistry in the world.

To secure this end in the opinion of your committee, a complete change is necessary in the policy which directs the Journal. The Journal has heretofore been regarded as primarily an outlet for the publication of industrial papers by our own members. It is highly improbable, for many well-recognized reasons, that for several years at least, a sufficient variety and number of high-class industrial papers can be secured from our own members to adequately present the march of development in industrial chemistry. It seems essential, therefore, that the Journal hereafter for some years, in any case, be edited almost wholly from the reader's standpoint.

In the opinion of your committee, it is obviously desirable that the conduct of the Journal be in the hands of an editor thoroughly in sympathy with the new policy suggested.

Your committee is further of opinion that articles for the Journal should be secured wherever possible, that a world-wide organization of reporters and correspondents be gradually built up, that reports of industrial processes and achievements be treated as news, as should also be treated the reports of meetings of chemical societies, great trade associations and scientific organizations everywhere, that the function of the journal should be that of impressing itself upon our membership rather than of affording a medium in which they may express themselves. It is believed that many of our younger members are almost wholly dependent upon the publications of the Society for their knowledge of current chemical achievement. The great majority of these younger men are working in the industrial field; to them, particularly, the Journal should be made a constant source of inspiration and enlightenment.

In the opinion of your committee, it is desirable that some other outlet be provided as early as possible for the large number of papers now presented on food, drug, analytical and agricultural chemistry. Much other material now appearing in the *Industrial Journal* might also be omitted to advantage. This refers to official rulings, government regulations and like material, readily available in full to any one. In case of such material, a mere reference to source and contents seems sufficient.

In conclusion, the committee desires to express its appreciation of the earnest and painstaking work of Dr. Richardson, which has resulted in the foundation and establishment of the *Journal of Industrial and Engineering Chemistry*. The value of this initial service can be in no way diminished by the change of editorial policy and larger development, which now seems desirable.

Respectfully submitted for the Committee,

A. D. LITTLE, *Chairman.*

W. D. Richardson then stated that he was not in sympathy with the report and requested that his name be not used for re-election. On nomination from the floor, M. C. Whitaker was elected Editor of the *Journal of Industrial and Engineering Chemistry*, and it was voted that the present Board of Associate Editors be continued for three months until the names of a new Board of Associate Editors recommended

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by the Editor-elect could be sent to the Council for election by letter ballot.

The meeting then adjourned. CHARLES L. PARSONS, *Secretary*.

MEMBERS ELECTED BETWEEN DEC. 15, 1910, AND JAN. 15, 1911.

Acton, Leonard T., c/o Continental Mexican Rubber Co., Torreon, Mexico.
Bennel, Roger F., 1307 E. Adams St., Syracuse, N. Y.
Bigelow, Harold E., 12 Oxford St., Cambridge, Mass.
Bingham, M. W., c/o James Pyle & Sons, Edgewater, N. J.
Bladen, Walter C., 185 So. 11th St., Newark, N. J.
Blatherwick, N. R., 604 Chalmers St., Champaign, Ill.
Bliss, Carl E., 2700 Mapledale Ave., Cleveland, Ohio.
Bolton, J. B., 1317 6th St., S. E., Minneapolis, Minn.
Boord, Cecil E., Chem. Dept., O. S. U., Columbus, Ohio.
Braddock, Homer F., Barclay Bldg., Greensburg, Penna.
Brehaut, Henry N., 37 Codman Park, Roxbury, Mass.
Brennesen, E. J., c/o Harlem Contracting Co., New York City.
Brodenik, Thomas, 2505 Portland Ave., So., Minneapolis, Minn.
Brown, (Miss) B. Marion, Simmons College, Boston, Mass.
Brown, George A., 10 Durham St., Boston, Mass.
Buvinger, Wilson J., No. 1 The Nelson, Walnut Hills, Cincinnati, Ohio.
Carpenter, Dwight C., 1213 N. Walnut St., Lansing, Mich.
Carver, B. F., 20 East 38th St., Bayonne, N. J.
Chapman, Richard H., Jr., 210 East Gravers Lane, Chestnut Hill, Philadelphia, Penna.
Chatfield, George F., Edgewater, N. J.
Childs, Lee E., Franklin, Ind.
Clark, Arthur W., 223 High St., Geneva, N. Y.
Clough, Harrison L., Merrimack, N. H.
Colebrook, M. W., Summerville Blvd., Irondequoit, N. Y.
Conn, Sterling C., 1525 Park Ave., Montreal, Canada.
Crauder, H. R., 315 So. Eastern Ave., Joliet, Ill.
Currie, James N., 608 W. Dayton St., Madison, Wisc.
Dahl, Alvin D., Midland, Mich.
Darling, Elton R., 601 Locust St., Fall River, Mass.
Dawkins, C. T., c/o Blast Furnace, Ashland, Wisc.
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BOARD OF DIRECTORS.

The Directors met in the Chemical Building, University of Minnesota, at 4 P.M., December 30th, with Directors Bancroft, Little, Love and Parsons present. President-elect Smith was also present on invitation.

It was voted that all recommendations of the Council with regard to financial matters as recorded in the minutes of the Council for December

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28th and December 29th are hereby approved and adopted as the action of the Board of Directors.

It was voted that the Editor-elect of the *Industrial Journal* be authorized to incur expenses which in his judgment are necessary to the successful conduct of the journal to an amount not in excess of fifteen hundred dollars above the budget quoted.

It was voted that the Editors of the Society's publications shall certify to the Finance Committee the amounts of bills due for extra reprints, together with the names of the parties to whom they should be sent, not including express charges, and that the Finance Committee having O.K.'d these bills, the Secretary shall collect same.

It was voted that the fittings and other similar property of the Society's Library which may be unnecessary to the Society in the new rooms to which they are to be moved be disposed of to the best advantage by E. G. Love, T. J. Parker and M. T. Bogert, and that they be empowered to draw up a contract with the Chemists' Club regarding the location of the Library in their new building and refer such contract to the Directors for action.

The meeting then adjourned. CHARLES L. PARSONS, *Secretary.*

MEETINGS OF THE SECTIONS.

[Full accounts of meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

CALIFORNIA SECTION.

The fifty-fourth meeting of the California Section took place at Bergez-Frank's Café, Saturday evening, November 19th. A paper of exceptional interest was presented by D. E. C. Burr, entitled "Some Men of Note." This referred to prominent chemists of the late sixties, who were either friends or teachers of Dr. Burr, and it was very interesting to hear about the men who helped pave the way to our present knowledge of chemistry and the recognition of its value to the industrial world.

The following officers were elected for the year 1911: *Chairman*, Ralph A. Gould; *Vice-Chairman*, F. T. Green; *Sec.-Treas.*, Chas. S. Ash; *Councilors*, M. E. Jaffa, E. C. Franklin.

The fifty-fifth regular meeting of the Section was held on Saturday evening, January 14th, at 8 o'clock, at Bergez & Frank's Café.

Mr. Mendeléeff, of the American Smelting and Refining Company, was our guest and kindly consented to address the Section.

CHARLES S. ASH, *Secretary.*

COLUMBUS SECTION.

There was a joint meeting of the Columbus Section and the Chemical Society of the Ohio State University on Friday evening, De-

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cember 9th, in Room 200, Chemistry Building, Ohio State University. The speaker of the evening was Dr. W. E. Henderson, Professor of Inorganic and Physical Chemistry, Ohio State University, and the subject was "Some Observations on European Education, Particularly as It Relates to Chemistry." Personal observations, especially of the German Universities, were narrated and discussed from the point of view of both professor and student.

JAMES R. WITHROW, *Secretary.*

UNIVERSITY OF MICHIGAN SECTION.

The Michigan Section held its annual meeting in the Chemical Building on Monday, Dec. 12th, Prof. Campbell in the chair and 18 members present. The society accepted the amendment to the charter, authorized by the Council of the American Chemical Society, Nov. 11th, 1910, and proceeded to reorganize as "The University of Michigan Section," with a territory restricted to an area within a radius of ten miles of the University of Michigan. The by-laws of the former Michigan Section were adopted, with the substitution of the word "chairman" for "presiding officer" in Section 1 of the By-laws. Officers were elected as follows: *Chairman*, M. Gomberg; *Secretary*, W. G. Smeaton, 1114 Prospect Street, Ann Arbor; *Councilor*, S. L. Bigelow.

WM. GABB SMEATON, *Secretary.*

SECTION OF WESTERN NEW YORK.

Additional Announcement.

The following papers were read at the meeting held on Dec. 14th: "Emulsification Wool Grease," by Mr. Hoppenstedt. "On the Simplification of Chemical Nomenclature," by Prof. Sy. "Glass Laboratory Burners," by R. E. Fowler. "Determination of Water and Soap," by Mr. Morey. "Monel Metal," by Mr. F. A. Lidbury.

Discussion followed by the above mentioned and also by Mr. Shed, Mr. W. H. Watkins, Prof. Bishop, Prof. Turner, Mr. Spaulding and Mr. Wallace.

W. WALLACE, *Secretary.*

NEBRASKA SECTION.

The 62nd regular meeting of the Section was held on Friday, December 16th, at 8 P.M., in the lecture room of the Chemistry Building of the University of Nebraska.

The program, which was very interesting, was as follows: "The Crucible Assay of Pyritic Concentrates for Gold and Silver," Prof. George Borrowman. "Prussic Acid in Corn," Mr. R. S. Trumbull. "Wheat Sampling and Nitrogen Determination," Mr. E. S. Bishop.

The following officers for 1911 were elected: *President*, Dr. H. A. Senter; *Vice-President*, Dr. F. J. Alway; *Councilor*, Chancellor Samuel Avery; *Sec.-Treas.*, Mr. C. J. Frankforter; *Executive Committee*, Dr. Benton Dales, Prof. George Borrowman, Mr. E. L. Redfern.

C. J. FRANKFORTER, *Secretary.*

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UNIVERSITY OF ILLINOIS SECTION.

The following papers were read at the meeting of the University of Illinois Section on Dec. 20th:

"The Removal of Iron from Water Supplies," by Prof. Edward Bartow. "Nitrogen Partition Data Collected from Two Men through a Seven-Day Fast, Following Prolonged Ingestion of a Low Protein Diet," by Dr. P. E. Howe.

GRINNELL JONES, *Secretary.*

PHILADELPHIA SECTION.

The regular December meeting of the Section was held on December 22nd, at the Engineers' Club, Philadelphia, the following program being presented:

"New Color Reactions for Some of the Resins with Halphen's Reagent for Colophony," by Edwin F. Hicks, Chief Chemist, Victor Talking Machine Co. Mr. Hicks showed that a large number of the resins give characteristic color reactions with this reagent and that it is especially sensitive and valuable as a test for rosin in shellac. "Report on Summer Meeting of the American Chemical Society at San Francisco," by Dr. A. M. Comey. Illustrated by numerous lantern slides.

The meeting was preceded by the usual dinner at the Engineers' Club.

CLEMENT S. BRINTON, *Secretary.*

NEW YORK SECTION.

The 4th regular meeting of the session of 1910–'11 was held at the Chemists' Club on January 6th.

Prof. Allen Rogers was elected to the vacancy made by Local Councilor E. G. Love becoming Councilor-at-Large.

The Nichols medal, awarded annually for the best paper read before the Section, was presented to M. A. Rosanoff and C. W. Easley for their paper "On the Partial Vapor Pressures of Binary Mixtures." President Wilder D. Bancroft made the presentation and Prof. Rosanoff replied on behalf of himself and Prof. Easley.

Mr. T. J. Parker gave an account of the Minneapolis meeting of the Society.

Dr. W. C. Moore read a paper by Prof. H. N. McCoy and himself on "Organic Amalgams." Prof. Robert Kennedy Duncan addressed the Section "On the Relation between Chemistry and Industry in America." Discussion of the subject followed by M. C. Whitaker, L. H. Baekeland and Allen Rogers.

C. M. JOYCE, *Secretary.*

ST. LOUIS SECTION.

At the January meeting of the Section, held on January 9th, Dr. Samuel H. Baer, of the Blanke-Baer Chemical Co., presented the first paper of the evening on "The Practical Study of Vanilla Beans." Professor E.

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H. Keiser spoke on "Synthetic Preparation of Fumaric and Maleic Acids from the Isomeric Acetylene Iodides." Dr. F. W. Frerichs spoke on "Chemical Engineering Education."

R. NORRIS SHREVE, *Secretary.*

CORNELL SECTION.

The January meeting was held on Jan. 10th, at 8 P.M., in Morse Hall, Lecture Room No. 1. The program consisted of an address on "Industrial Organization," by Prof. D. S. Kimball.

Light refreshments were served after the meeting.

J. C. ANDREWS, *Secretary.*

CINCINNATI SECTION.

The 165th regular meeting of this Section was held at the Ohio Mechanics Institute on Wednesday, January 11th, at 8 P.M.

The paper for the evening, entitled "The Present Status of the Fixation of Nitrogen," was read by Dr. Henry Max Goettsch. Dr. H. S. Fry read by title a paper on "The Constitution of Naphthalene from the Standpoint of the Electronic Conception of Positive and Negative Valencies. (1) The Dynamic Formulae and Ultraviolet Absorption Spectrum of Naphthalene."

ALFRED SMITH, *Recording Secretary.*

WISCONSIN SECTION.

The January meeting of the Section was held at Madison on Wednesday, January 11th, at 8 P.M., in Room 113 of the Chemistry Building.

J. H. Mathews spoke on "The Heat of Reaction between Pyridine and Acetic Acid in Various Solvents, and a New Method for Determining Heats of Neutralization," and O. L. Kowalke on "Some Problems in Gas Calorimetry."

W. G. WILCOX, *Secretary.*

WASHINGTON SECTION.

The 203rd meeting was held at the Cosmos Club, Thursday, January 12th, at 8 P.M.

The following papers were presented: "The Importance of the Polypeptides to Biological Chemistry," A. H. Koelker (J. H. Univ.). "The Sulphides of Iron," E. T. Allen, J. L. Crenshaw and J. Johnston (Geophysical Lab.). "Phosphate Deposits of Florida,'" W. H. Waggaman (Bur. Soils).

J. A. LECLERC, *Secretary.*

SECTION OF EASTERN NEW YORK.

The first meeting of 1911 was held in Schenectady at the Chemical Laboratory of Union College on Friday, Jan. 13th, at 8.15 P.M. The program was as follows:

"Recent Advances in Our Knowledge of the Laws of Radiation and its Application in the Measurement of High Temperatures," by Dr. Irving Langmuir.

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"Report of Minneapolis Meeting," by Dr. W. R. Whitney.

Preceding the meeting an informal dinner was held at the Hotel Vendome.

G. R. FONDA, *Secretary.*

SYRACUSE SECTION.

Dr. L. L. Van Slyke spoke on the Work of the State Agricultural Experiment Station, Friday, January 13th, at 8 P. M., at the Medical College.

WM. H. MCLAUCHLAN, *Secretary.*

CHICAGO SECTION.

The Section held the January meeting as guests of the Chicago Section of the American Electrochemical Society, in the rooms of the Western Society of Engineers, on Friday evening, January 20th, at 8 o'clock.

The general subject of the evening was "Electric Steel Making," and the following papers were presented:

"Electric Furnaces for the Manufacture of Iron and Steel," by Mr. James Lyman, District Engineer General Electric Co. "Reliability of Electric Furnaces for Commercial Work," by Mr. F. T. Snyder, Metallurgic Engineering Co. "Electric Refining as a Step in the Production of Steel," by Mr. C. F. Burgess, Professor of Chemical Engineering, University of Wisconsin. "Some Experiments with Electric Furnaces at South Chicago," by Mr. Chas. E. Osborne, Superintendent of Special Steels, Illinois Steel Co., South Works. General discussion followed.

The installation of new officers took place immediately after the dinner, which was held at the Grand Pacific Hotel. There were 87 present at the dinner and 200 at the meeting.

D. K. FRENCH, *Secretary.*

DECEASED MEMBERS.

Robert A. Duncan, Honolulu, Hawaii.

Rudolph Fittig.[1]

After a brief illness Rudolph Fittig died November 19, 1910. He was born at Hamburg, Germany, December 6, 1835, and was therefore nearly seventy-five years old at the time of his death. Fittig studied at Göttingen from 1856 to 1859. The moving spirit in the Göttingen laboratory at that time was, of course, Wöhler, whose chief interest was in inorganic chemistry. Limpricht had general charge of organic chemistry, and it was under him that Fittig did most of his work. Among his contemporaries were Beilstein and Hübner. When Limpricht went to Greifswald, Beilstein had already gone to St. Petersburg, and this left the two young men, Fitting and Hübner, to take care of organic chemistry. Fittig became Privatdocent in 1860, and in 1868 he was made Professor *extraordinarius*. In 1870 he was called to Tübingen to take the place of Strecker, who had gone to Würzburg. He remained at Tübingen until 1876, when he accepted the professorship of chemistry

[1] Presented at the Minneapolis meeting of the American Chemical Society, December 30, 1910.

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in the University of Strassburg as the successor of Von Baeyer, who had been called to Munich. He performed the duties of the professorship in Strassburg until 1902, when he retired from active service, though he continued to live in Strassburg and occupied himself in rounding out his extensive investigations and preparing the results for publication. His work never stopped until his death as far as the outside world can judge.

Fittig began his career as an investigator by some observations on acetone. He soon became interested in the aromatic compounds which were then coming into prominence. Nothing of much importance came of his work, however, until 1864, when his famous article, "The Synthesis of Methyl-phenyl by the Wurtz Method," appeared in the *Annalen der Chemie*, 131, 303. Tollens was associated with him in this piece of work and the article appeared under both names. Benzene had then been known for a number of years, but no helpful suggestion had up to that time been made regarding its relation to the paraffins. Toluene was also known and had received its place next to benzene in the aromatic series, but the relation between benzene and toluene was not at all clear to the chemists of that day. That the two differed from each other in composition as the successive members of an homologous series differ from each other was recognized, but the nature of homology was still a subject of discussion, and the question whether the then known toluene was a true homolog of benzene was unanswered. Wurtz had devised a method of synthesis for the paraffins which has proved of great value in clearing up the relations between these hydrocarbons, and it occurred to Fittig to apply this method to the aromatic hydrocarbons. He first treated monobromebenzene with sodium and found that the bromine is easily removed, and that the two phenyl groups thus formed unite to form diphenyl:

$$2C_6H_5Br + 2Na = C_6H_5 — C_6H_5 + 2NaBr.$$

The fact having been established that sodium has the power to remove the bromine from monobromobenzene, he next tried the action of sodium on a mixture of monobromobenzene and methyl bromide. The reaction took place as was expected and a compound to which Fittig and Tollens gave the name methylphenyl was formed:

$$C_6H_5Br + CH_3Br + 2Na = C_6H_5 — CH_3 + 2NaBr.$$

They showed that their synthetical product was identical with toluene, and in discussing the result they used these words: "Accordingly toluene is benzene in which the radical methyl has been substituted for an atom of hydrogen." * * * "Toluene is generally regarded as the second member of the benzene series, that is to say, as a true homolog of benzene. If this view is correct, the possibility is given of building

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up an homologous series from the initial member by means of such synthetical experiments, and, we may say in general, that one substance is homologous to another, if in place of hydrogen in its radical it contains the radical methyl. Before, however, we can accept such a view in regard to the constitution of homologous compounds as correct, the question must first be answered, whether toluene really is a homolog of benzene, whether it bears to benzene the same relation, that, for example, ethyl compounds bear to methyl compounds. The conduct of the two hydrocarbons as far as it is at present known is well calculated to give a negative rather than a positive answer to the question."

This passage is very interesting historically, as it helps us to understand how our present clear-cut view of homology came to be accepted. Very shortly after the appearance of the article by Fittig and Tollens, Schorlemmer[1] showed that the compound made by extracting the chlorine from methyl chloride is identical with "ethyl hydride," that it is in fact ethane, the second member of the paraffin series. This result, taken together with that obtained by Fittig and Tollens, left no doubt in regard to the nature of homology, and since that time it has been glibly defined, with little thought, generally speaking, as to how the explanation was reached. Fittig seems soon to have lost his doubts regarding the homology of toluene and benzene.

In 1886, Kekulé, in his famous article[2] on aromatic compounds, refers to Fittig's work thus: "The beautiful investigations of Fittig leave no room for doubt in regard to the constitution of these hydrocarbons." And much later, in 1890, when the German Chemical Society celebrated the 25th anniversary of the birth of his benzene theory, Kekulé again refers to Fittig's work. He tells of the way his theory of the constitution of chemical compounds came to him in a half-dreamy state, and how he had put aside what he had written on this subject at that time. He adds: "The same thing happened with the benzene theory. It lay nearly a year, written out among my papers, until the beautiful syntheses of the aromatic hydrocarbons by Fittig and Tollens led me to publish what I had written."

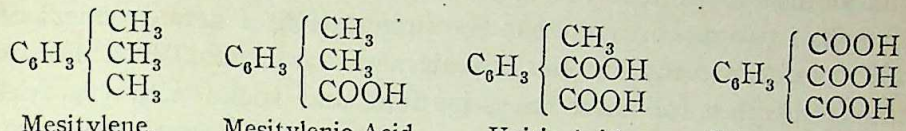
The next important contribution of Fittig was one which showed mesitylene to be a trimethyl derivative of benzene. The two articles embodying the results of the investigation on mesitylene appeared in the *Annalen* in 1867 and 1868. He showed that by oxidation mesitylene yields successively a monobasic, a dibasic, and a tribasic acid, and that each stage involves the conversion of one methyl group into a carboxyl. From the tribasic acid by distillation with lime benzene is formed, from the dibasic acid toluene is formed in the same way, and from the mono-

[1] *Ann. Chem.* [Liebig], 132, 234.
[2] *Ibid.*, 137, 141.

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basic acid one of the xylenes. He says: "It follows, however, from these facts that mesitylene is a true trimethyl-benzene, and that the following constitutional formulas must be assigned to the principal members of the mesitylene series:



Mesitylene. Mesitylenic Acid. Uvitic Acid. Trimesitic Acid.

Later it was shown that mesitylene is the symmetrical variety of trimethyl-benzene and, that being established, it follows that the xylene obtained from mesitylenic acid must be the meta variety, and this becomes one of the foundation stones upon which the classification of the di-substitution products of benzene into ortho, meta, and para rests.

It will be quite impossible to discuss all of Fittig's work as the two important contributions above referred to have been discussed. Indeed it is doubtful whether anything he did in the years after 1868 had as much influence on chemical thought as that which he did before this time.

It has already been stated that he was called to Tübingen in 1870. There he found conditions somewhat unfavorable. He had to do more lecturing and the laboratory was a sorry affair. Fittig had the most fastidious tastes so far as his laboratory surroundings were concerned. He was extremely neat and orderly. In Tübingen things looked down at the heel and this seemed to worry him constantly. Nevertheless, he went on with his work and accomplished much. During the six years of his life here he was rather feeling his way. Nothing very striking came of it. His work on phenanthrene led him to the view that the quinones are diketones and this view prevails at present. An investigation on sorbic acid and another on piperic acid interested him in unsaturated acids and these continued to occupy him several years. The results are embodied in a series of articles entitled "Untersuchungen über die ungesättigen Säuren," the first of which appeared in the *Annalen* in 1877 and the last in 1883.

His discovery of the lactones and the lactonic acids was announced in 1880 and a number of comprehensive articles on these compounds followed, extending to 1893.

His studies of the unsaturated acids led, among other things, to the interesting observations that some of these acids are subject to an internal change involving a "shifting of the double bond."

By invitation of the German Chemical Society he gave a general account of his work on the unsaturated acids before the Society, October 15, 1894. The address was published in the *Berichte*, **27**, 2658. He tells of an interesting way how he came to take up this work and in general what object he had in view. The following characteristic passage may be

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quoted to advantage. He says: "My colleagues have repeatedly said to me that it is difficult to work through my bulky articles, and I believe many have asked, whether it was necessary to collect such a mass of material and always to test the same reaction in so many special cases. Gentlemen, I can assure you that the preparation of new chemical compounds has never in my life had any attraction for me. When, however, I formed the plan for these investigations and spoke with my friends about it, I knew very well that the carrying out of the plan would require many years, for it was perfectly clear to me that no generalizations could be reached through the study of a few cases."

At the beginning of Fittig's work the field of the unsaturated acids was almost uncultivated. He has enriched it with almost innumerable discoveries and it has yielded an abundant harvest.

Fittig's work was characterized by great thoroughness and accuracy and he justly prided himself upon the fact that no one had ever convicted him of an experimental error! There was, to be sure, a painful polemic between him and Wislicenus in regard to the bromine addition product of angelic acid, but it turned out that the difference between the results obtained by the two observers was due to the fact that one worked on the south side of his laboratory, the other on the north side, and the light proved to be the determining factor in the reaction.

Fittig did not directly contribute to any extent to the theories of chemistry, though he furnished the material basis for profitable speculation, notably, as has been pointed out, in his earliest work on aromatic compounds. It is doubtful whether any text-book of chemistry has ever been written that had less reference to underlying theories than his "Grundriss der anorganischen Chemie" and his editions of "Wöhler's Grundriss der organischen Chemie." These books are made up of compact statements of facts and are extremely valuable for the purpose for which they were prepared. He was a clear lecturer and an excellent laboratory teacher. His insistence upon thoroughness was characteristic of everything he did, and those who had the privilege of working under him have every reason to be thankful for the influence exerted by him as a teacher.

The writer of this sketch was closely associated with Fittig for four years, two years as a student at Göttingen and two years as an assistant at Tübingen, and he always recalls these years with gratitude, conscious of the fact that this association played a large part in such intellectual regeneration as he has been permitted to experience.

IRA REMSEN.

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A UNIVERSAL LAW.[1]

BY WILDER D. BANCROFT.

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Now that we appreciate fully that physics, geology, engineering, physiology, medicine, botany, zoology, and biology are subdivisions of the broader science of chemistry, we see that the chemist of the future must know a great deal more than any of us now do, if he is to keep in touch with the whole subject. Many people believe that this is impossible and that the scientific man of the future will be a narrow specialist, knowing only a small part of a single division of one science. I do not believe this. As we look back over the history of any science, we see always two opposing tendencies, one that complicates and one that simplifies. The discovery of new facts makes a subject more complex and more difficult to grasp. The discovery of new relations simplifies matters because it enables us to correlate facts and thus to get a better grasp of the subject.[2]

In the chemistry of to-day we have three, great, simplifying generalizations which are familiar to all of you: the atomic theory, the periodic law, and the phase rule. These have long since proved their value as a means of correlating facts and as working hypotheses enabling us to predict new facts. The value of these is not great, however, when we get beyond what is called chemistry in the narrower sense of the word.

As one universal law we have the great, simplifying generalization known as the Law of the Conservation of Energy. The marvelous effect of this in enabling one to correlate and remember apparently unrelated facts was brought out in a most striking way in Kundt's lectures on physics.

[1] Presidential address delivered at the Minneapolis meeting of the American Chemical Society, December 28, 1910.

[2] Cf. Bancroft, *J. Elisha Mitchell Soc.*, 20, 39 (1904).

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I wish to call your attention to-night to what I believe to be another universal law, a qualitative one and not a quantitative one. The chemists call it the Theorem of Le Chatelier. The physicists call it the Theorem of De Maupertuis or the Principle of Least Action. By the biologists it is known as the Law of the Survival of the Fittest, while the business man speaks of the Law of Supply and Demand. The broadest definition of it is that a system tends to change so as to minimize an external disturbance.

In chemistry proper and in physics we study chiefly the effects of temperature, pressure, concentrations, electricity, and light; but in the natural history sciences we must also take account of moisture, food and fertilizers, secretions, climate, etc.

If we heat a liquid we convert a portion of the liquid into vapor, an operation which absorbs heat. If we heat a saturated solution, the solubility increases if the solid dissolves with an absorption of heat. If we increase the pressure on a dissociating compound or if we increase the concentration of the dissociation products, we get a decrease of dissociation which involves a decrease in pressure and a decrease in the amount of the dissociation product. If we pass an electric current through a solution, we tend to get a counter-electromotive force which cuts down the electrical stress. If we have suspended particles in a liquid, a difference of potential causes them to move in the direction which reduces the electrical stress. Since all substances absorb light of some wave length to a greater or lesser extent, all substances are light-sensitive to some rays and tend to change in such a way as to eliminate the strain caused by the light. Whether any measurable change takes place, depends on other conditions. With some silver salts or with Eder's solution of mercuric oxalate, we get visible decomposition. With chromium salts we get no measurable change unless some reducing agent is present. With some substances we get fluorescence or phosphorescence but ordinarily without apparent change. With copper sulfate solution there is apparently no effect due to light. Yet all these solutions are really light-sensitive and they all tend to change in the same way, namely, to eliminate the substance which absorbs the light.

In the business world, continuous over-production of any commodity necessitates a fall in the price of the article. Also, a sufficiently widespread and prolonged decrease in the demand for meat will bring down the price, at least temporarily. This may not help the consumer, because he may have to pay more for fish, eggs, and vegetables; but that is not our problem.

If one should ship enough copper abroad as export copper and should bring it back as ballast, one would create a state of strain which would eventually play havoc with the price of copper. It is said that this ex-

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periment was tried when the price of copper was over twenty cents; but the details have never been published. Over-production of silver destroyed the ratio of sixteen to one, while over-production of gold is now said to be one of the factors in the high cost of living.

In physiology and medicine we find many illustrations of our law. "When irritating substances get into the eye, a flow of tears occurs to wash them away; from the nose and respiratory passages, they are ejected by sneezing or by cough; and from the stomach or intestines, they are removed by the vomiting and purging to which they themselves give rise."[1]

If a splinter lodges in one's finger and is not removed, festering occurs and the splinter is sloughed out. The throwing off of a cold is merely the elimination by the system of the disturbing factors and the same may be said about the recovery from any disease. Herter[2] says that "disease is generally the expression of a reaction on the part of the cell to injurious influences."

When studying chemical reactions, we find some cases, such as the inversion of sugar, in which the reaction products have little or no effect on the reaction. In many other cases, the reaction may come to an end if the reaction products are not removed. In these latter cases the reaction products might be said to be toxic to the system. Analogous cases occur in physiology. Some secretions or reaction products are not toxic to the system while others are. Brunton[3] says that "cells excrete poisons formed within their bodies... [and that] an excessive quantity of their own products is usually injurious to cells." We all know that the waste products of digestion must be removed from the intestines periodically or poisoning will ensue, and we also know that the system tends to react in such a way as to remove these products.

In the cases thus far considered, it has been fairly clear what the response of the system would be; but this is not always so. If a man goes out into the street and slaps another man's face, he creates a state of strain, which may be relieved by the other man's running away. It is quite possible, however, that the other man may knock the first man down, or he may hand the first man over to a policeman, if one happens to be near. What happens depends on the relative sizes and temperaments of the two men and on the nearness of the policeman. We cannot make A, B, and C represent the first man, the other man, and the policeman, and then interchange the letters. We have the same thing in mixtures of three liquids. If we add one liquid to another, we always lower the vapor pressure of the second to a certain extent. We cannot

[1] Brunton, *St. Louis Congress of Arts and Sciences*, 6, 176 (1904).
[2] *Chemical Pathology*, 2 (1902).
[3] *St. Louis Congress of Arts and Sciences*, 6, 174 (1904).

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make any such definite statement about what will happen if we add a third liquid to the other two. The addition of the third liquid may decrease the partial pressures of both the other liquids or it may decrease the partial pressure of either one and increase that of the other. We must know the specific properties of the liquids before we can predict what will happen.

We know that an irritating substance is often removed from the stomach by vomiting; but if we administer poison continuously for a long time, the system tends to eliminate the irritating effect by becoming immune to the poison. We need not hark back to the mythical case of Mithridates who qualified for the throne by living on all the known poisons while young. The case of the arsenic eaters is better authenticated.[1] The whole of immunochemistry is an illustration of the applicability of our law.[2]

The most interesting field for the study of our law is to be found in the natural history sciences. Here we must consider the survival of the race as well as the survival of the individual or we shall make serious mistakes. Thus plants and trees often flower at an abnormal time after receiving serious injury.[3] This is really one form of tendency to eliminate the disturbing factor. One should also distinguish between the direct injury to the plant or animal and the change in the organism which enables it or its descendants to withstand the disturbing influences.

A great deal has been done in the way of collecting facts illustrating the effect of environment on plants and animals; but the real reason for any particular change is rarely given,[4] and the change is only too often the resultant of two or more factors which are not differentiated carefully. I am going to cite some cases in which the application of the Theorem of Le Chatelier is quite clear, and also others which seem interesting enough to warrant attention being called to them.

Pressure and Concentration.

The wind blows against the trees and the boughs bend so as to spill the wind. A prevailing wind from a given direction causes the trees to assume a permanent set. This is not especially interesting because this change is probably not inherited to any appreciable extent.

Bailey[5] has pointed out that plants tend to become circular instead of bilateral, because they are sessile. "They, therefore, found it to their advantage to reach out in every direction from their support in the search for food. While the centrifugal arrangement has strongly tended to

[1] Brunton, *St. Louis Congress of Arts and Sciences*, 6, 177 (1904).

[2] Cf. Le Dantec, *La Stabilité de la Vie*, 25 (1910).

[3] Cf. Möbius, *Lehre von der Foripflanzung der Gewächse*, 6, 122 (1897).

[4] Cf. Bailey, *The Survival of the Unlike*, 32 (1896); McDougal, *Memoirs N. Y. Bot. Garden*, 2, 1 (1903); Crozier, *The Modification of Plants by Climate* (1885); Eimer, *Organic Evolution* (1890).

[5] *The Survival of the Unlike*, 15 (1896).

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disappear in the animal creation, it has tended with equal strength to persist and to augment itself in the plant creation. Its marked development among plants began with the acquirement of terrestrial life, and with the consequent evolution of the asexual or sporophytic type of vegetation. Normally, the higher type of plant bears its parts more or less equally upon all sides, and the limit to growth is still determined by the immediate environment of the given individual or of its recent ancestors. Its evolution has been acephalic, diffuse, or headless, and the individual plant or tree has no proper concentration of parts. For the most part it is filled with unspecialized plasma, which, when removed from the parent individual (as in cuttings or grafts), is able to reproduce another like individual. The arrangements of leaves, branches, the parts of the flower, and even of the seeds in the fruit, are thus rotate or circular, and in the highest type of plants the annual increments of growth are disposed in like fashion; and it is significant to observe that in the compositae, which is considered to be the latest and highest type of plant-form, the rotate or centrifugal arrangement is most emphatically developed. The circular arrangement of parts is the typical one for higher plants and any departure from this form is a specialization, and demands explanation."

In England, rabbits are held in check, though with some difficulty. If the repressive factors are removed, as in Australia, the rabbits adapt themselves to the situation and multiply so as to become a veritable pest. In the same way the Russian thistle spread through the Northwest some years ago. An insect will often adapt itself to changed conditions to such an extent as to take on new habits.[1] "An early naturalist, traveling in Colorado, found a striped beetle feeding upon wild solanums or nightshades. The insect came to be in demand among collectors, and it is said that handsome prices were paid for specimens for museums. In the course of time the settlers grew potatoes in Colorado and the insect took a fancy to them and spread rapidly. It is now known as the Colorado potato-beetle. The first attacks were noticed about thirty years ago, but now the insect is a serious pest wherever potatoes are grown in quantity."

The displacement of equilibrium due to cultivating large areas to one crop has led to an enormous increase in the number of insects and fungous enemies in any given region.[2]

"The excessive ravages of insects in the United States are largely owing to the cultivation of their food-plants in extended areas. Two hundred years ago not even the wild crab, the earliest representative of the apple, existed in this country, and consequently there were no

[1] Cf. Bailey, *The Survival of the Unlike*, 184 (1896).

[2] Lintner, *First Report State Entom. N. Y.*, 10 (1882).

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apple insects. Later when a few apple trees became the adjunct of the simple homes of the early settlers, those of our insects to which they offered more desirable food than that on which they had previously subsisted were obliged to wing their way often for many miles in search of a tree on which to deposit their eggs. If birds were then abundant, how few of the insects could accomplish such extended flights! But in the apple orchards of the present day—some of them spreading in almost unbroken mass of foliage over hundreds of acres—our numerous apple insects may find the thrifty root, the vigorous trunk, the succulent twig, the tender bud, the juicy leaf, the fragrant blossom, and the crisp fruit spread out before them in broad array, as if it were a special offering to insect voracity, or a banquet purposely extending an irresistible invitation.....Careful cultivation has made it the best of its kind; appetite is stimulated; development is hastened; broods are increased in number; individuals are multiplied beyond the conservation of parasitic destruction; facilities of distribution are afforded with hardly a proper exercise of locomotive organs; and when these almost useless members have become absorbed, as in the wingless females of the bark-louse and the canker-worms, the interlocking branches afford convenient passage from tree to tree."

As Bailey[1] says: "We, as horticulturists, are every year planting new invitations to insect and fungous attacks. If we take this extra risk, we must certainly prepare ourselves to meet it. Our fathers' weapons cannot avail against the horde of invaders which we are inviting to our doors. They are coming up out of the woods and the swamps and the bare fields to regale themselves at the banquet which we have spread.

"*Cultivation affords places of less struggle than organisms are forced to occupy under normal conditions.* Man disturbs the equilibrium or removes the pressure in some direction, and a multitude is waiting to spring into the void. The great potato fields not only provided food, but there were few other insects to dispute the possession of them; the Colorado solanum beetle saw his opportunity, and improved it. He has been a successful bug. This release of the natural tension, which cultivation affords, is to my mind the most potent factor in the increase of our little foes."

Temperature.

One effect of a lower temperature is obviously to produce a better protective coating on animals, while a higher temperature acts in the opposite way. I quote a few special cases from Darwin.[2]

"According to Roulin, the semi-feral pigs in the hot valleys of New Granada are very scantily clothed; whereas on the Paramos, at the height

[1] *The Survival of the Unlike*, 187 (1898).

[2] *Animals and Plants under Domestication*, 2nd Ed., 1, 81, 95, 102 (1890).

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of 7000 to 8000 feet, they acquire a thick covering of wool lying under the bristles, like that on the truly wild pigs of France."

"Roulin asserts that the hides of the feral cattle on the hot Llanos are always much less heavy than those of the cattle raised on the high platform of Bogotá; and that these hides yield in weight and in thickness of hair to those of the cattle which have run wild on the lofty Paramos. The same difference has been observed in the hides of cattle reared on the bleak Falkland Islands and on the temperate Pampas."

"Great heat seems to act directly on the fleece: several accounts have been published of the change which sheep imported from Europe undergo in the West Indies. Dr. Nicholson, of Antigua, informs me that, after the third generation, the wool disappears from the whole body, except over the loins; and the animal then appears like a goat with a dirty door-mat on its back. A similar change is said to take place on the west coast of Africa. On the other hand, many wool-bearing sheep live on the hot plains of India. Roulin asserts that in the lower and heated valleys of the Cordillera, if the lambs are sheared as soon as the wool has grown to a certain thickness, all goes on afterwards as usual; but if not sheared, the wool detaches in flakes, and short shining hair like that of a goat is produced ever afterwards. This curious result seems merely to be an exaggerated tendency natural to the Merino breed, for, as a great authority, namely Lord Somerville, remarks, 'the wool of our Merino sheep after shear time is hard and coarse to such a degree as to render it almost impossible to suppose that the same animal could bear wool so opposite in quality, compared to that which has been clipped from it; as the cold weather advances, the fleeces recover their soft quality.' As in the sheep of all breeds the fleece naturally consists of longer and coarser hair covering shorter and softer wool, the change which it often undergoes in hot climates is probably merely a case of unequal development, for even with those sheep, which like goats are covered with hair, a small quantity of underlying wool may always be found. In the wild mountain sheep (*Ovis montana*) of North America there is an analogous change of coat;[1] the wool begins to drop out in early spring, leaving in its place a coat of pelage quite different in character from the ordinary thickening—for instance in the horse, the cow, etc., which shed their winter coat in the spring."

The fact of there being wool-bearing sheep in the hot plains of India is not necessarily a contradiction of the general law, because the tendency to change may be counteracted by careful selection.[2] "M. Lasterye, after discussing this subject, sums up as follows: The preservation of the Merino race in its utmost purity at the Cape of Good Hope, in the

[1] Audubon and Bachman, *The Quadrupeds of North America*, 5, 365 (1846).

[2] Darwin, *Animals and Plants under Domestication*, 2nd Ed., 1, 103 (1890).

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marshes of Holland, and under the rigorous climate of Sweden, furnishes an additional support of this my principle, that fine-wooled sheep may be kept wherever industrious men and intelligent breeders exist."

If we remove a plant to a climate where frosts occur earlier, the chances are very good that the plant will be killed before the seeds ripen. If the variety is to survive, an early-ripening form must develop. This actually happens with wheat.[1]

"Wheat quickly assumes new habits of life. The summer and winter kinds were classed by Linnaeus as distinct species; but M. Monnier has proved that the difference between them is only temporary. He sowed winter-wheat in the spring, and out of one hundred plants four alone produced ripe seeds; these were sown and resown, and in three years plants were reared which ripened all their seed. Conversely, nearly all plants raised from summer-wheat, which was sown in autumn, perished from frost; but a few were saved and produced seed, and in three years this summer-variety was converted into a winter-variety. Hence it is not surprising that wheat soon becomes to a certain extent acclimatized, and that seed brought from distant countries and sown in Europe vegetates at first or even for a considerable period, differently from our European varieties. In Canada the first settlers, according to Kalm, found their winters too severe for winter-wheat brought from France, and their summers often too short for summer-wheat, and they thought that their country was useless for corn crops until they procured summer-wheat from the northern part of Europe, which succeeded well."

Another interesting case is that of corn, also cited by Darwin.[2] "The tall kinds grown in southern latitudes, and therefore exposed to great heat, require from six to seven months to ripen their seed; whereas the dwarf kinds, grown in northern and colder climates, require only from three to four months. Peter Kalm, who particularly attended to this plant, says, that in the United States in proceeding from south to north, the plants steadily diminish in bulk. Seeds brought from lat. 37° in Virginia, and sown in lat. 43°–44° in New England, produce plants which will not ripen their seed, or ripen them with utmost difficulty. So it is with seed carried from New England to lat. 45°–47° in Canada. By taking great care at first, the southern kinds after some years' culture ripened their seed perfectly in their northern homes, so that this is an analogous case with that of the conversion of summer- into winter-wheat, and conversely. When tall and dwarf maize are planted together, the dwarf kinds are in full flower before the others have produced a single flower, and in Pennsylvania they ripen their seeds six weeks earlier than the tall maize. Metzger also mentions a European maize which ripens

[1] Darwin, *Animals and Plants under Domestication*, 2nd Ed., 1, 333 (1890).
[2] *Animals and Plants under Domestication*, 2nd Ed., 1, 341 (1890).

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its seed four weeks earlier than another European kind. With these facts so plainly showing inherited acclimatization, we may readily believe Kalm, who states that in North America maize and some other plants have gradually been cultivated further and further northward."

The peach tree offers another good instance of acclimatization.[1]

"Mr. Crozier records testimony to the effect that peach trees in Michigan were injured no more at a temperature of twenty degrees below zero than they were in central Mississippi at a temperature of zero. Peach buds are injured at a much higher temperature at the south than at the north. Mr. P. H. Mell, Jr., director of the Alabama Polytechnic Institute at Auburn writes me that buds are often killed even at a temperature of 34 to 38 degrees above zero. This observation undoubtedly refers to the partially expanded buds, yet it is well known that at the north a considerable frost is required to kill the swelling buds. It is possible that all these instances of the peach should fall under the division of adaptation through modification of individual constitution; but as I cannot be certain, if indeed it is probable, that all these cases represent bud offspring, I place the statement here. If trees of the same variety show this difference in different latitudes, as they undoubtedly often do, then we have indisputable evidence of the acclimatizing of the individual."

Bailey's quotation from Cooper as to watermelons also has a bearing on this matter.[2]

"A striking instance of plants being naturalized, happened by Colonel Matlack sending some watermelon seed from Georgia, which, he informed me [Cooper] by letter, were of superior quality. Knowing that seed from vegetables which had grown in more southern climates, required a longer summer than what grew here, I gave them the most favorable situation, and used glasses to bring them forward, yet very few ripened to perfection; but finding them to be so excellent in quality as described, I saved seed from those first ripe; and by continuing that practice four or five years, they became as early watermelons as I ever had."

Changes in the colors of some butterflies can be obtained by varying the temperature during the pupal stage of development. While we are not able to prove that these changes are beneficial adaptations, it is interesting to note that these changes characterize the same butterflies in arctic and tropic regions.[3]

"Warmth acting on pupae of *V. cardui* (painted lady), gave an extraordinarily pale form, like those found in very different parts of the tropics. Cold, on the other hand, gave specimens with a very recog-

[1] Bailey, *The Survival of the Unlike*, 325 (1896).

[2] *Ibid.*, 154 (1896).

[3] Vernon, *Variations in Plants and Animals*, 237 (1903).

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nizable darkening of the whole insect, such as is exhibited by a form found in Lapland."

We have no clue[1] at all as to the influence a low temperature has upon the production of wings in *Aphides*. "As long as the temperature is high and the moisture sufficient, plant lice are wingless; but if the temperature be lowered, wings begin to grow." The problem is an interesting one and should not be difficult to solve with the aid of the Theorem of Le Chatelier.

Light.

Since light tends to destroy any substance which absorbs it, it seems at first sight as though transparent, colorless plants and animals would be the surviving type in the intense light of the tropics. Light does tend to bleach organic colors; but the flaw in the reasoning is that we are dealing with living organisms.[2] It is easier for a man or an animal to develop a pigmented coating and thus eliminate the chemical action of light on blood[3] than for it to acquire the habit of living without red corpuscles. It is evidently better for a plant to develop chlorophyll and a healthy appetite for carbon dioxide than for it to be bleached by the light.

"Consequently we find that man is invariably covered with a pigment which acts as an armor to exclude the more harmful short rays, and moreover the amount of pigment is in direct proportion to the intensity of the light of the country to which his ancestors have proved their adjustment by centuries or millenniums of survival in health and vigor. It is a simple matter of mathematics to show that the intensity of light under the zenith sun in the tropics is the greatest, and that the amount of rays per unit of surface diminishes as we go north in proportion to a function of the latitude. In addition to this, the further from the tropics we go the greater is the layer of air which the rays must pass through and the more of them which are absorbed. Hence we can reach a latitude where there is insufficient light for plant growth even if there could be sufficient warmth. Yet man flourishes in these regions, and so do other animals. Hence we find the greatest pigment in the tropics among the Australians, New Guineas, Negritos, East Indians, and African Negroes, some of whom are nearly jet-black. As we go north from the tropics we find the complexions gradually lightening, being dark brown in Egypt, light brown in North African States, deep olive in the Mediterranean, olive in southern Europe, brunette in Central Europe, and blonde in the northwestern section of Europe, embraced by a curve passing through Northern France, Northern Germany, and Northwest Russia.

[1] Loeb, *The Dynamics of Living Matter*, 112 (1908).
[2] Cf. Eimer, *Organic Evolution* 136 (1890).
[3] Cf. Woodruff, *Effects of Tropical Light on White Men*, 10, 85 (1905).

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"Undoubtedly the negro, while in the shade, is able to radiate heat better than whites, and this enables him to keep cool in the tropics, but puts him at a disadvantage in the north where the white man can keep warmer with less clothing and less fire in the house. But it is a secondary cause enhancing the first, because when it comes to a question of light and cold, nature makes no mistakes, but selects a color able to exclude the light. Hence in all cold, light countries, *i. e.*, steppes, plains, and the arctics, there is a pigmentation of a color in the lower end of the spectrum, red or yellow, with variations of brown, olive or copper. As a rule the color is markedly light yellow in cold, light countries, as in North China.

"In America we had every shade from the blackest Indians of tropical South America through all the shades of copper and brown to the very light, almost white Indians of the northeastern part of the United States, who had conditions very similar to those suited for the blondes of Europe. In Italy, Spain, and China, we find the same thing, for the men of the south are markedly darker than those of the north.

"The same law holds in France, Germany, Russia, Persia, and India: the north is decidedly blonder than the south, and the same is found in the British Islands, but in a much modified way. Even the Ainos in the north of Japan are said to be lighter than the Japanese.

"All these red and yellow colors undoubtedly enable the native to conserve his heat almost as well as the white man, and at the same time exclude the dangerous short waves."

In Africa, Eimer[1] found that in passing up the Nile valley from the Delta to the Soudan, the natives gradually became more and more dark-skinned, the further south they lived.

Woodruff[2] recommends that white men in the tropics should wear white outer gaments and black underclothes, which constitutes a pretty fair imitation of a dark-skinned Arab in a white burnous.

Vernon[3] points out "that the diminution or disappearance of pigmentation following upon withdrawal of light is best illustrated by reference to the well-known cave animals. Of these, one of the most interesting is *Proteus anguineus*, which is found in the subterranean caves of the Karst mountains about Adelsberg. This amphibian is almost white, but if kept for some time in the light, it gradually becomes pigmented. Pigment cells are, in fact, still present in its skin, and in all probability these are directly stimulated to exert their function by the action of the light." If Vernon had been familiar with the Theorem of Le Chatelier, he would have worded this last sentence very differently.

In the case of heliotropism, the animals turn automatically to or from

[1] *Organic Evolution*, 88 (1890).
[2] *Effects of Tropical Light on White Men*, 321 (1905).
[3] *Variation in Animals and Plants*, 250 (1903).

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the source of light, depending on whether they are positively or negatively heliotropic. In some cases they also move automatically towards or away from the light. Loeb[1] says in regard to this:

"This automatic orientation is determined by two factors, first a peculiar photo-sensitiveness of the retina (or skin), and second a peculiar nervous connection between the retina and the muscular apparatus. In symmetrically built heliotropic animals in which the symmetrical muscles participate equally in locomotion the symmetrical muscles work with equal energy as long as the photo-chemical processes in both eyes are identical. If, however, one eye is struck by stronger light than the other, the symmetrical muscles will work unequally and in positively heliotropic animals those muscles will work with greater energy which bring the plane of symmetry back into the direction of the rays of light and the head towards the source. As soon as both eyes are struck by the rays of light at the same angle, there is no more reason for the animal to deviate from this direction and it will move in a straight line. All this holds good on the supposition that the animals are exposed to only one source of light and are very sensitive to light."

Loeb[2] has also shown that the heliotropism may sometimes be modified or even reversed by adding certain chemicals to the water. He has also shown[3] that some animals seek automatically the places where the intensity of light is a minimum, but that this is not negative heliotropism because the animals do not necessarily move along the path of the ray. In all these cases we have an application of our law, because the animals arrange themselves so as to minimize the state of stress.

It had always seemed to me a most mysterious thing that animals should be heliotropic, until it finally dawned on me that we are all of us heliotropic to a certain extent. Place a man out in an intense light and, if he cannot shade his eyes, it will take a pretty strong special stimulus to keep him from turning his back to the light. If his eyes happen to be weak, he will respond more promptly and more automatically to the light. He is negatively heliotropic to strong light. I am inclined to think that man is positively heliotropic to a faint light, because he would certainly tend to turn towards the point that he could see. We can also find an analogy to the case of the animals which congregated at the places where the intensity of light is a minimum. Place a man out on the desert in blazing sunlight and it will take a strong counter-stimulus to keep him from moving into any shade that he can find. Here the irritation is due to heat and not to light; but the man is not negatively

[1] *Darwin and Modern Science*, 264 (1909).

[2] *The Dynamics of Living Matter*, 131 (1906); *Darwin and Modern Science*, 265, (1909).

[3] Loeb, *The Dynamics of Living Matter*, 136 (1906).

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thermotropic because he will move across the temperature gradient in order to reach the shade.

Of course the reflex action is not relatively so powerful with man as with the lower animals. In fact, Loeb[1] says that "it rarely happens that animals endowed with the mechanisms of associated memory react in such a machine-like manner to the elementary forces of nature as the heliotropic animals which we have discussed."

Vernon[2] points out that "if plants be allowed to grow in absolute darkness, they, as a rule, become very much elongated in form while their leaves are small and ill-shaped.....Sachs found that potato tubers grown in darkness for fifty-three days produced sprouts from 150 to 200 mm. high, while similar ones grown in daylight were only 10 to 13 mm. high. Again he found that the hypocotyl of the buckwheat (*Fagopyrum*) reached a height of 35 to 40 cm. in the dark, while it grew only to 2 or 3 cm. when freely exposed to light. K. Goebel has shown that if cactuses are cultivated in darkness, their form changes completely. The young shoots are rounded, and fail to show the angular irregularities of form which increase the surface capable of effecting assimilation under the influence of light."

Since the leaves especially are effective in the light, the absence of light will prevent normal development of the leaves and this seems to be the chief direct effect. If the plant does not have to develop leaves to any extent, there is more food available for the stem and the growth of the stem is thus really a secondary effect. The matter is still further complicated by the fact that the moisture content and the carbon dioxide content of the air were not kept constant during the two sets of experiments.

An increase in the intensity of the light is often accompanied by a decrease in the surface of the leaf and an increase in the thickness.[3] I think that it is a mistake to attribute this change to the action of light alone. It is more the combined effect of light and dryness, or of light and the higher rate of evaporation due to a higher temperature. With decreased surface and greater thickness there is less evaporation, one extreme of which is reached in the eucalyptus with its leaves turned edgewise. The assimilation of food is provided for by an increased thickness of the chlorophyll layer, because the more intense light can penetrate farther into the leaf.

We have seen that the pigment in the negro's skin is essentially protective in action. A thicker or coarser leaf may also be a protection against too intense a light. Rowlee[4] found that "intense light does

[1] *The Dynamics of Living Matter*, 135 (1906).

[2] *Variation in Animals and Plants*, 245 (1903).

[3] Vernon, *Ibid.*, 248 (1903).

[4] *Proc. 19th Meeting Soc. Promotion Agr. Science*, Boston (1898).

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not kill thick, coriaceous, or succulent leaves with heavy cutinized external walls...doubtless owing to the screening effect of the heavy walls of cells containing much water."

We have not sufficient data to make it possible to say why an increase in the intensity of light causes the change from sexual to asexual reproduction in some algae and the reverse change in others;[1] but we can be quite certain that both changes are in conformity with the Theorem of Le Chatelier.

Moisture.

Vernon[2] says that "the effect of a dry soil and atmosphere is well shown by the characters of desert plants. These are stunted in growth, and are of a nearly uniform gray color, owing to their intense hairiness. The leaves are more fleshy, and there is a great tendency to the formation of spines. That these characters are, in part at least, the direct result of want of water is shown by the fact that they may disappear if water is supplied." The development of hairs is of great advantage to a plant in an arid climate, especially if there is any wind. The circulation of air, and consequently the rate of evaporation is impeded by the mass of hairs.

We get characteristic changes when plants, normally terrestrial, are grown in water.[3] "As regards the leaves, it is well known that when aërial and floating leaves are present on the same aquatic plant, they differ greatly in structure, and as a rule also in form, from the submerged leaves. In *Ranunculus heterophyllus* and *Cabomba aquatica*, for instance, the floating leaves are more or less rounded, while the submerged ones have dissected and filiform segments. In *Hippuris* (mare's-tail), the aërial and floating leaves are short, and in *Callitriche* rounded, but the submerged leaves of both are linear or ribbon-like. In all cases the submerged leaves are of a more delicate texture, more or less translucent, and of a brighter green color than the others."

This is a much more complex case than Vernon realizes. Submerged leaves do not develop the supporting frame of the aërial leaves. The delicate texture is, therefore, to a great extent a result of the supporting power of the water and not of its wetness. Since the supporting structure of the aërial leaf is not developed when the leaf is submerged, the leaf grows longer, just as the stem of the plant grows longer in the dark, because the leaves develop but slightly. The thinness of the leaf is probably chiefly a result of the decreased intensity of light. This is the best analysis that can be given at present, but it brings out clearly how slack people have been in controlling conditions.

[1] Loeb, *Darwin and Modern Science*, 230 (1909).
[2] *Variation in Animals and Plants*, 263 (1903).
[3] Cf. Vernon, *Ibid.*, 266 (1903).

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The effect of excessive moisture or aridity upon plants is similar in type[1] to the effect of heat or cold on the pupae of butterflies.

"The relation of leaf-form to environment has often been investigated and is well known. The leaves of bog and water plants afford the most striking examples of modifications: according as they are grown in water, moist or dry air, the form of the species characteristic of the particular habitat is produced, since the stems are also modified. To the same group of phenomena belongs the modification of the forms of leaves and stems in plants on transplantation from the plains to the mountains or *vice versa*. Such variations are by no means isolated examples. All plants exhibit a definite alteration in form as the result of prolonged cultivation in moist or dry air, in strong or feeble light or in darkness, or in salt solutions of different composition and strength."

The last sentence in the preceding paragraph is interesting for what it does not say. There is no indication that Klebs has any inkling of the universal law underlying all these changes.

Food and Fertilizers.

It seems evident that an exuberant growth would be favorable to variability and to the development of sports. This is universally recognized to be the case. Thus Darwin[2] says: "Of all the causes which induce variability, excess of food, whether or not changed in nature, is probably the most powerful. This view was held with regard to plants by Andrew Knight and is now held by Schleiden, more especially in reference to the inorganic elements of the food. In order to give a plant more food, it suffices in most cases to grow it separately, and thus prevent other plants robbing its roots. It is surprising, as I have often seen, how vigorously our common wild species flourish when planted by themselves, though not in highly manured land; separate growth is, in fact, the first step in cultivation. We see the converse of the belief that excess of food induces variability in the following statement by a great raiser of seeds of all kinds. 'It is a rule, invariably with us, when we desire to keep a true stock of any one kind of seed, to grow it on poor land without dung; but when we grow for quantity we act contrary, and sometimes have dearly to repent of it.' According, also to Carrière, who had great experience with flower-garden seeds, *'On remarque en général les plantes de vigeur moyenne sont celles qui conservent le mieux leurs caractères.'* "

Under the heading of effect of cultivation, Klebs[3] says: "It is however a fact that if a plant is removed from natural conditions into cultivation, a well marked variation occurs. The well-known plant breeder,

[1] Klebs, *Darwin and Modern Science*, 235 (1909).

[2] *Animals and Plants under Domestication*, 2nd Ed., 2, 244 (1890).

[3] *Darwin and Modern Science*, 245 (1909).

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L. de Vilmorin, speaking from his own experience, states that a plant is induced to *affoler*, that is to exhibit all possible variations from which the breeder may make a further selection only after cultivation for several generations. The effect of cultivation was particularly striking in *Veronica chamaedrys*, which, in spite of its wide distribution in nature, varies very little. After a few years of cultivation this 'good' and constant species becomes highly variable. The specimens on which the experiments were made were three modified inflorescence cuttings, the parent plants of which certainly exhibited no striking abnormalities. In a short time many hitherto latent potentialities became apparent, so that characters, never previously observed, or at least very rarely, were exhibited, such as scattered leaf-arrangement, torsion, terminal or branched inflorescences, the conversion of the inflorescence into foliage-shoots, every conceivable alteration in the color of flowers, the proliferation of flowers."

One more quotation will suffice, this time from Bailey.[1]

"Now let us endeavor to put ourselves in nature's place, if such a conception is possible, and to briefly follow an outline of her methods with plants. We shall find that variation is largely the result, so far as we can see, of excess of food supply. The seedsman knows that heavy lands make his seed-crops break into non-typical forms, and he therefore prefers, for most plants, a soil not very rich in nitrogen or growth production. Heavy soils make the dwarf peas 'viney,' and bud sprouts of curious leaves and flowers are wont to appear upon over-vigorous shoots."

Since conditions which tend to shorten the life of a plant or tree often cause the plant or tree to flower,[2] it follows that conditions which favor a rank growth are likely to be disadvantageous to the production of flowers. This is actually the case.[3]

"One extreme case, that of exceptionally early flowering, has been observed in nature and more often in cultivation. A number of plants under certain conditions are able to flower soon after germination. This shortening of the period of development is exhibited in the most striking form in trees, as in the oak,[4] flowering seedlings of which have been observed from one to three years old, whereas normally the tree does not flower until it is sixty or eighty years old.

"Another extreme case is represented by prolonged vegetative growth leading to the complete suppression of flower production. The result may be obtained with several plants, such as *Glechoma*, the sugar beet,

[1] *The Survival of the Unlike*, 169 (1898).

[2] Möbius, *Beiträge zur Lehre von der Fortpflanzung der Gewächse*, 7, 125 (1897).

[3] Klebs, *Darwin and Modern Science*, 232, 246 (1909).

[4] Möbius, *Beiträge zur Lehre von der Fortpflanzung der Gewächse*, 89 (1897). [The conditions are not given by Möbius—W. D. B.]

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Digitalis, and others, if they are kept during the winter in a warm, damp atmosphere, and in rich soil: in the following spring or summer they fail to flower. Theoretically, however, experiments are of greater importance in which the production of flowers is inhibited by very favorable conditions of nutrition occurring at the normal flowering period. Even in the case of plants of *Sempervivum* several years old, which, as is shown by control experiments on precisely similar plants, are on the point of flowering, flowering is rendered impossible if they are forced to very vigorous growth by an abundant supply of water and salts in the spring. Flowering, however, occurs, if such plants are cultivated in relatively dry soil and in the presence of strong light. Careful researches into the conditions of growth have led, in the case of *Sempervivum*, to the following results: (1) With a strong light and vigorous carbon-assimilation in strong light, a considerably increased supply of water and nutritive salts produces active vegetative growth. (2) With vigorous carbon assimilation in strong light, and a decrease in the supply of water and salts, active flower production is induced. (3) If an average supply of water and salts is given both processes are possible; the intensity of carbon assimilation determines which of the two is manifested. A diminution in the production of organic substances, particularly of carbohydrates, induces vegetative growth. This can be effected by culture in feeble light or in light deprived of the yellow-red ray; on the other hand, flower-production follows increase in light intensity. These results are essentially in agreement with well-known observations on cultivated plants, according to which, the application of much moisture, after a plentiful supply of manure composed of inorganic salts, hinders the flower-production of many vegetables, while a decrease in the supply of water and salts favors flowering."

"Good manuring is in the highest degree favorable to vegetative growth, but is in no way equally favorable to the formation of flowers. The constantly repeated expression, good or favorable nourishment, is not only vague but misleading, because circumstances favorable to growth differ from those which promote reproduction; for the production of every form there are certain favorable conditions of nourishment, which may be defined for each species. Experience shows that, within definite and often very wide limits, it does not depend on the *absolute amount* of the various food substances but upon their respective degrees of concentration. As we have already stated, the production of flowers follows a relative increase in the amount of carbohydrates formed in the presence of light as compared with the inorganic salts on which the formation of albuminous substances depends.[1] The various modifications of flowers are due to the fact that a relatively too strong solution

[1] Klebs, *Künstliche Metamorphosen*, 117.

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of salts is supplied to the rudiments of these organs. As a general rule every plant form depends upon a certain relation between different chemical substances in the cells and is modified by an alteration of that relation."

Vernon[1] cites some interesting cases in which changes of diet have apparently produced results in accordance with our law.

"John Hunter observed a most marked thickening and hardening in the stomach of a gull (*Larus tridactylus*) which had been fed for a year on grain. It is stated by Dr. Edmonston that a similar change takes place under natural conditions every year in the stomach of the common herring gull (*Larus argentatus*). Thus in the Shetland Islands, this bird feeds in the winter on fish, but in the summer frequents the corn-fields and feeds on grain. Dr. Edmonston has also noticed a somewhat similar change in the stomach of a raven which had been fed for a long time on vegetable food. Again, Menetries found that in an owl (*Strix gallaria*) the effect of vegetable diet was to change the form of the stomach and make the inner coat leathery.

"The converse experiment of feeding graminivorous birds on a flesh diet has been made by Dr. Holmgren. By feeding pigeons on meat for a considerable time, he found that the gizzard gradually acquired the qualities of a carnivorous stomach. Again Delage fed a fowl for three years on meat, and found that the muscular substance of its gizzard was considerably decreased. All these results, though apparently so unequivocal, have not passed unchallenged; for G. Brandes[2] who fed both flesh-feeding birds on grain, and grain-feeders on flesh states that he was unable to trace any adaption to the altered conditions in either case."

Since these alleged changes are directly in line with the cases, previously quoted, of the changes in butterflies and bog plants, it seems probable that the negative results are due to error. It is very desirable, however, that this point should be settled definitely one way or the other.

A very complicated case of the effect of the environment, and one which I shall not attempt to account for, is cited by Poulton.[3]

"Entirely new light upon the seasonal appearance of epigamic characters is shed by the recent researches of C. W. Beebe,[4] who caused the scarlet tanager (*Piranga eythromelas*) and the bobolink (*Dolichonyx oryzivorous*) to retain their breeding plumage through the whole year by means of fattening food, dim illumination, and reduced activity. Gradual restoration to the light and the addition of meal-worms to the diet invariably brought back the spring song, even in the middle of winter. A sudden

[1] *Variation in Animals and Plants*, 295 (1903).
[2] *Biol. Centralblatt*, 16, 825.
[3] *Darwin and Modern Science*, 297 (1909).
[4] *The American Naturalist*, 42, 34 (1908).

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alteration of temperature, either higher or lower, caused the birds nearly to stop feeding, and one tanager lost weight rapidly and in two weeks moulted into the olive-green winter plumage. After a year, and at the beginning of the normal breeding season, 'individual tanagers and bobolinks were gradually brought under normal conditions and activities,' and in every case moulted from nuptial plumage to nuptial plumage. 'The dull colors of the winter season had been skipped.' The author justly claims to have established that the sequence of plumage in these birds is not in any way predestined through inheritance...., but it may be interrupted by certain factors in the environmental complex."

Secretions.

Under physiology and medicine mention has previously been made that many organisms give rise to products which are toxic to the organism and which must be removed. Brunton[1] points out that "an excessive quantity of their own products is usually injurious to cells and too much alcohol will stop the growth of yeast. At the same time these products are frequently very nutritious for cells of a different sort and alcohol furnishes a most suitable pabulum for the organisms which produce vinegar. Vinegar in its turn is toxic to the microbe which produces it, but serves again as a soil for another which gives rise to a viscous fermentation. By the successive action of these ferments a solution of sugar may produce, first, alcohol, secondly, vinegar and thirdly, ropy mucus. In this particular series each microbe produces a substance injurious to itself but useful to its successor. This is, however, not always the case, because a cell may produce a substance not only injurious to itself but injurious to other cells, and alcohol in large quantity not only kills the cells of yeast, but other cells as well. Similar conditions occur within living organisms where the cells composing the different parts are connected together and pass on the products of their life from one cell to another by means of the circulation of the blood and tissue juices. The secretions of one part may be, and indeed generally are, useful to other parts of the organism and so long as no part sins, either by deficiency or excessive action, the whole organism maintains a condition of health. But this is not always the case and health may be destroyed by (*a*) excessive, (*b*) defective, or (*c*) prevented action of one or more of the parts composing the body."

Vernon[2] has tested the influence of the excreta of adult echinoids upon larval growth. "Echinoids of known weight were kept for a known time in a known volume of water, so that on determining the absolute effect produced on larvae grown in this water it was possible to calculate the relative effect produced by unit weight of echinoids kept for unit

[1] *Darwin and Modern Science*, 174 (1909).
[2] *Variation in Animals and Plants*, 298 (1903).

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time in unit volume of water. On growing larvae in water previously fouled by adult echinoids of their own species, it was found that, as a means of five observations, they were diminished in relative size by 2.6 per cent., while only 41 per cent. of the ova employed reached the larval stage. On growing them in water fouled by echinoids of other than their own species, the larvae, as a mean of five observations, were diminished by only 1.9 per cent., while 54 per cent. of the ova reached the larval stage; that is to say, the products of excretion of an echinoid act more adversely both on the death-rate and on the growth of embryos if these belong to its own species than if they belong to another species. At least this is the case with *Strongylocentrotus*, *Sphaerechinus*, and *Echinus*. With two other (physiologically) less closely related species, *viz.*, *Arbacia pustulosa* and *Dorocidaris papillata*, it was even found that the products of excretion, so far from acting adversely on growth, actually favored it. Thus *Strongylocentrotus* larvae grown in water fouled by these two species were increased in size by respectively 4.3 and 1.7 per cent., while respectively 81 and 50 per cent. of the ova employed reached the pluteus stage."

Vernon[1] points out also that "De Varigny actually found that snails grown in water in which other snails had already been growing several months were distinctly smaller than those grown in fresh water, and if the excreta of snails had been added as well, they were smaller still."

The experiments of Warren[2] show that water fouled by *Daphnia* becomes specifically injurious to *Daphnia*, "for when the *Daphnia* are fast disappearing, there may be a swarm of ostracods or copepods (still living healthily in the water)."

If we were to reason from these facts to the behavior of crops, such as wheat for instance, we should conclude that wheat unquestionably secretes substances which are toxic to itself and that the development of that crop or of a subsequent one would depend in part on the degree of the accumulation of the toxic substances in the soil. If the toxic substances were removed or destroyed sufficiently rapidly, no deleterious result would occur, but, otherwise, there would be one. We should also conclude that the secretions from the wheat would not necessarily be toxic to other crops. These *a priori* predictions seem to be confirmed by the facts.

Cameron[3] points out that "it has been found that as a general rule the continued growth of one crop in any soil results in a low crop production. Pot cultures have given even more pronounced results in the same direction. The explanation long accepted is that the soil has, as a result of

[1] *Variation in Animals and Plants*, 305 (1903).
[2] Vernon, *Ibid.*, 309 (1903).
[3] *J. Phys. Chem.*, 14, 425 (1910).

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the continued cropping, become deficient in one or more of the 'available,' mineral nutrients. Pot experiments, where the garnered crop was returned to the soil and still diminished yield was obtained, throw doubt on this explanation. Still further doubt results from water cultures which, by growing a crop in them, become 'poor' for subsequent crops, although there is maintained in them an ample supply of mineral plant nutrients, and they are easily renovated by good adsorbers. These facts find a more satisfactory explanation as being due to the production in the nutrient medium of deleterious organic substances originating in the growing plant itself. This idea seems to have been advanced first by De Candolle, in 1832, to account for the beneficial results obtained by employing a rotation of crops. It appears to have been held by Liebig at one time, although he subsequently abandoned it in favor of the view that the benefits of a crop rotation are due to the several crops requiring different proportions of mineral nutrients, that the disturbance of the balance in the soil produced by one crop is not unfavorable to the growth of some other crop. Although lacking direct experimental confirmation, this latter view of Liebig's has long prevailed among agricultural investigators, partly by reason of his authority, partly by reason of the dominance of the plant-food theory of fertilizers, and partly by reason of the fact that the ideas of De Candolle, as originally advanced, include certain errors soon detected. The trend of recent investigations has been distinctly in favor of a modified form of the view of De Candolle. It has been recognized that other factors enter into crop rotations such as the elimination of associated weeds, various kinds of animal, insect and plant parasites, preparation of the soil by a deep-rooted crop for a shallow-rooted following crop, etc. It has come to be recognized that there are natural associations of plants and natural rotations of vegetation certainly determined by other than plant-food factors. Thus, in the eastern United States, wheat is followed by ragweed naturally, while across the fence cocklebur and wild sunflowers come in after the corn, the difference in vegetation being as sharply marked after the removal of the crops as when they still occupied the land. Analyses of the ragweed, for instance, although it is a shallower rooted crop than wheat, show that it takes from the soil as much of the mineral nutrients as does the preceding wheat crop. The investigation of Lawes and Gilbert on fairy rings showed that the continual widening of the rings cannot be satisfactorily explained by the comparison of the mineral constituents in the soil within and without the rings. Work at Woburn on the effect of grass on apple trees finds no other plausible explanation than that the growing grass produces in the soil organic substances detrimental to young apple trees. A number of similar cases have been recorded."

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Climate.

When seeds are planted in a new locality, a great many conditions are varied simultaneously and it is difficult, usually impossible, to tell to what extent each factor causes the changes that actually take place or why any given change is beneficial. If we compare two varieties of the same plant, it seems reasonable to suppose, unless proof to the contrary is given, that the local variety is fairly well adapted to the local conditions, in which case one would expect the foreign variety to vary towards the local one. Darwin[1] cites a case of this sort.

"The effect of the climate of Europe on the American varieties [of maize] is highly remarkable. Metzger obtained seed from various parts of America, and cultivated several kinds in Germany. I will give an abstract of the changes observed in one case, namely with a tall kind (*Breit-körniger Mais, Zea altissima*) brought from the warmer parts of America. During the first year the plants were twelve feet high, and a few seeds were perfected; the lower seeds in the ear kept true to their proper form, but the upper seeds became slightly changed. In the second generation the plants were from nine to ten feet in height, and ripened their seed better; the depression on the outer side of the seed had almost disappeared, and the original beautiful white color had become duskier. Some of the seeds had even become yellow and in their now rounded form they approached common European maize. In the third generation nearly all resemblance to the original and very distinct American parent-form was lost. In the sixth generation this maize perfectly resembled a European variety, described as the second sub-variety of the fifth race. When Metzger published his book, this variety was still cultivated near Heidelberg, and could be distinguished from the common kind only by a somewhat more vigorous growth..."

Bailey[2] draws the following conclusion in regard to American fruits and American climate. "American fruits constantly tend to diverge from the foreign types which were their parents, and they are, as a rule, better adapted to our environments than foreign varieties are. In less than a century we have departed widely from the imported varieties which gave us a start. At the expiration of another century we should stand upon a basis which is nearly if not wholly American."

Darwin[3] notes a similar case. "Mr. Meehan has compared twenty-nine kinds of American trees with their nearest European allies, all grown in close proximity and under as near as possible the same conditions. In the American species he finds, with the rarest exceptions, that the leaves fall earlier in the season and assume before their fall a brighter

[1] *Animals and Plants under Domestication*, 2nd Ed., 1, 340 (1890).
[2] *The Survival of the Unlike*, 319 (1898).
[3] *Animals and Plants under Domestication*, 2nd Ed., 2, 271 (1890).

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Wilder D. Bancroft

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tint; that they are less deeply toothed or serrated; that the buds are smaller; that the trees are more diffuse in growth and have fewer branchlets; and, lastly, that the seeds are smaller—all in comparison with the corresponding European species. Now considering that these corresponding trees belong to different orders, and that they are adapted to widely different stations, *it can hardly be supposed that their differences are of any special service to them in the New and Old Worlds*;[1] and, if so, such differences can not have been gained through natural selection, and must be attributed to the long-continued action of a different climate."

As a matter of fact, most of these changes are just what would be beneficial in a country having a hot, dry summer with a relatively long winter. If planted in a very moist place, the American elm develops some of the characteristics of the English elm.

Woodruff[2] has pointed out one marked case of adaptation to climate. "The shape and size of the nose and position of the nostrils are now fairly well proved to be a matter of selection of fittest variations. In the tropics where the air is hot and therefore rarefied, more of it is necessary and it is essential that there should be no impediment to the air currents, so that the nostrils are open and wide and the nose very flat. Such a nose is unsuited for cold countries as it permits masses of cold air to flood the air passages and irritates the lining membrane, so that the nose must be large and have much warming surface, and the nostrils therefore are slender slits to admit the air in thin ribbons easily warmed. The air being cold is concentrated, and less of it is needed than in the tropics and the slender nostril is no disadvantage. The nasal index or extreme width of nose divided by the extreme length, gradually increases as we go to warmer countries, where we find some races with nose index much greater than one thousand, *i. e.*, width greater than length. It is now many years since it was first pointed out that the open tropical nostril was one reason for so much pulmonary trouble of negroes out of the tropics. Hence there must have been a natural selection in cold countries of one kind of variations—large concentrated noses, and a selection in hot countries of the other extreme, so that the various types gradually arose.

"The great Biblical Pharaoh Rameses II had a prominent slender nose not now found in any Egyptians, and it is a positive proof of the recent arrival of some ancestor from the north. He was like Lord Cromer —a northern type ruling a native type."

Allen[3] has called attention to a correlation between climate and the color of birds. "The increase in color towards the south coincides with

[1] [The italics are mine.—W. D. B.]

[2] *Effects of Tropical Light on White Men*, 4 (1905).

[3] Vernon, *Variation in Animals and Plants*, 327 (1903).

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the increase in the intensity of the sun's rays and in the humidity of the climate. The increase in color observed in birds on passing from east to west (in the United States) seems also to coincide with an increase of humidity, 'the darker representatives of any species occurring where the annual rainfall is greatest, and the palest where it is least.' This coincidence occurs not only in the birds of the United States to such a degree that Allen says he knows of no exception, but in Europe also. Thus birds from the Scandinavian coast are very much darker than in central Europe where the rainfall is only half as great. Allen says that this correlation of brighter and deeper tint with increased humidity is exhibited by the mammals of these districts, as well as by the birds."

Nonadaptability.

While the Theorem of Le Chatelier enables us to account for the direction of a change, it does not tell us whether a given stimulus will actually produce a change or under what condition the change will be a maximum for the same stimulus. We can make a fair guess at the answer by studying ourselves. We know that, as we get older, our tendency to resist change increases; our habits of body and mind become more fixed. We should, therefore, be tempted to conclude that the resistance to change increases as the organism becomes mature and that a given stimulus would probably have the most effect if applied at or before the earliest stages of development. The following quotation from Vernon[1] would seem to indicate that this was often true.

"Due reflection, will, I believe, incline one to infer that what is true for echinoid larvae is true for most multicellular organisms. In fact, it would seem to be a law of general application that the permanent *effect of environment on the growth of a developing organism diminishes rapidly and regularly from the time of impregnation onwards*.

"It is curious that this principle, enunciated by the author in 1900, should have been laid down by De Vries only a few months later, as the result of his observations on plants. Thus, judging from the effects of nutrition (manuring, planting out, good light and watering), he concluded that: (1) the younger a plant is, so much the greater is the influence of external conditions on its variability. (2) The nutrition of the seed, when developing on the maternal plant, has—at least very often—a greater influence on the variability than nutrition during its germination and later growth."

If the pressure on a liquid is made less than the vapor pressure for that liquid at that temperature, some of the liquid vaporizes, the temperature falls, and the liquid may be said to adapt itself to the new conditions. What would happen if the liquid were not adaptable? The easiest way to obtain a nonadaptable liquid is to place a Bunsen burner

[1] *Variation in Animals and Plants*, 199 (1903).

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under it. The temperature rises until the boiling point is reached. The liquid then ceases to be adaptable. It volatilizes, it disappears, it becomes extinct so far as that particular region or flask is concerned. If a species cannot adapt itself to changed climate or other conditions, it does not volatilize; but it disappears, it becomes extinct. It may be a new point of view to consider the extinction of the mastodon as analogous to the distillation of water; but the two cases are really parallel, except in time.

It should be kept in mind that nonadaptability is not the only cause for extinction. A species might have enormous potential adaptability; but it would become extinct if the death-rate were too high in comparison with the rate of adaptation. This principle is made use of in the fight against weeds.[1]

"Weeds, like other plants, grow where they can find room; and the more room any plant can find, other things being the same, the farther and more rapidly it will spread over the earth. But room, used in this connection, does not mean, entirely, space vacant of other plants, but rather conditions of competition into which the given plant can fit itself with prosperity. Ground may be covered with a given plant, and yet a species of wholly different character and habits may thrive along with it. This is well illustrated in the growth of twining or climbing vines in dense thickets of shrubbery, or the practice, common even with the Indians, of growing pumpkins in cornfields. If weeds, then, are to be kept out of grounds, the land must not only be occupied with some other crops, but with a crop which will not allow the weed to grow along with it. In practice, it is impossible to select all crops from plants which so completely encumber the ground that no intruder can find a foothold; but this disadvantage is readily and almost wholly overcome by means of the rotation of crops—one crop in the rotation destroying what weeds may have crept in with the preceding ones. Thorough cropping of the land and judicious rotation of crops, therefore, are conditions against which no weeds can stand; and as these are the vital conditions, also, of successful agriculture, it may be said that weeds are never serious when lands are well farmed.

"The daisy-cursed meadows of the east are those which have been long mown and are badly 'run,' or else those which were not properly made, and the grass obtained but a poor start. The farmer may say that the daisies have 'run out' the grass, but the fact is that the meadow began to fail, and the daisies quickly seized upon the opportunity to gain a foothold; and just so long as the farmer persists in his accustomed methods, will the daisies usurp the land. The weedy lawns are those which have a thin turf, and the best treatment is to scratch the ground

[1] Cf. Bailey, *The Survival of the Unlike*, 194, 196 (1896).

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lightly with an iron-toothed rake, apply fertilizer and sow more seed; in other words, augment the struggle for existence, and the weeds will go down before the June grass, and the grass plants themselves, because of the greater numbers, will be more slender and will make a softer turf."

Attitude of Biologists.

It may be asked to what extent biologists make use of the Theorem of Le Chatelier as a working hypothesis in studying the effect of external conditions. So far as I can learn, nobody makes any active use of it, and many biologists would deny the applicability of the theorem.

Darwin[1] began by attributing very little to the direct action of the climate, etc.; but later he stated that more weight should have been allowed to the direct action of the environment, *i. e.*, food, climate, etc., independently of natural selection. He says[2] that it is "probable that variability is directly or indirectly caused by changed conditions of life. Or to put the case under another point of view, if it were possible to expose all the individuals of a species during many generations to absolutely uniform conditions of life, there would be no variability." In spite of this he states[3] explicitly that long-continued action of a different climate has produced differences in American trees which are of no especial service to them.

Nägeli's[4] "extensive cultural experiments with alpine *Hieracia* led him to form the opinion that the changes which are induced by an alteration in the food-supply, in climate or in habitat, are not inherited and are, therefore, of no importance from the point of view of the production of species."

De Vries[5] is distinctly not prepared to admit that mutations are described by the Theorem of Le Chatelier.

"The origin of new species, which is in part the effect of mutability, is, however, due mainly to natural selection. Mutability provides the new characters and new elementary species; natural selection, on the other hand, decides what is to live and what to die. Mutability seems to be free, and not restricted to previously determined lines. Selection, however, may take place along the same main lines in the course of long geological epochs, thus directing the development of large branches of the animal and vegetable kingdom. In natural selection it is evident that nutrition and environment are the main factors. But it is probable that, while nutrition may be one of the main causes of mutability, environment may play the chief part in the decisions ascribed to natural selection. Relations to neighboring plants and to injurious or useful

[1] Cf. Schwalbe, *Darwin and Modern Science*, 125 (1909).
[2] Darwin, *Animals and Plants under Domestication*, 2nd Ed., 2, 242 (1890).
[3] Darwin, *Ibid.*, 2nd Ed., 2, 271 (1890).
[4] Cf. Klebs, *Darwin and Modern Science*, 225 (1909).
[5] *Darwin and Modern Science*, 77 (1909).

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animals have been considered the most important determining factors ever since the time when Darwin pointed out their prevailing influence."

There is nothing very definite to be obtained from Klebs.[1]

"The dependence of *variable internal* on *variable external* condition gives us the key with which research may open the door. In the lower plants this dependence is at once apparent, each cell is directly subject to external influences. In the higher plants with their different organs, these influences were transmitted to cells in course of development along exceedingly complex lines. In the case of the growing point of a bud, which is capable of producing a complete plant, direct influences play a much less important part than those exerted through other organs, particularly through the roots and leaves, which are essential in nutrition. These correlations, as we may call them, are of the greatest importance as aids to an understanding of form-production. When a bud is produced on a particular part of a plant, it undergoes internal modifications induced by the influence of other organs, the activity of which is governed by the environment, and as the result of this it develops along a certain direction; it may, for example, become a flower. This particular direction of development is determined before the rudiment is differentiated and is exerted so strongly that further development ensues without interruption, even though the external conditions vary considerably and exert a positively inimical influence; this produces the impression that development proceeds entirely independently of the outer world. The wide-spread belief that such independence exists is very premature and at all events unproven.

"The state of the young rudiment is the outcome of previous influences of the external world communicated through other organs. Experiments show that in certain cases, if the efficiency of roots and leaves as organs concerned with nutrition is interfered with, the production of flowers is affected, and their characters which are normally very constant undergo far-reaching modifications. To find the right moment at which to make the necessary alteration in the environment is indeed difficult and in many cases not yet possible. This is especially the case with fertilized eggs, which in a higher degree than buds have acquired, through parental influences, an apparently fixed internal organization, and this seems to have predetermined their development. It is, however, highly probable that it will be possible, by influencing the parents, to alter the internal organization and to switch off development on to other lines."

Bailey is quite clear that the environment has a marked effect upon plants; but he is very far from formulating that effect, as the following quotations will show.[2]

[1] *Darwin and Modern Science*, 228, 235, 242 (1909).

[2] Bailey, *The Survival of the Unlike*, 32, 309 (1896).

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"These differences [between individual plants] arise as a result of every impinging force—soil, weather, climate, food, training, conflict with fellows, the strain and stress of wind and wave, and insect visitors—as a complex resultant of many antecedent external forces, the effects of crossing, and also as the result of the accumulated force of mere growth; they are indefinite, non-designed, an expression of all the various influences to which the passive vegetable organism is or has been exposed; these differences which are most unlike their fellows or their parents find the places of least conflict and persist because they thrive best, and thereby impress themselves best upon their offspring."

"It is not too much to ask of climatology that it shall tell us why the northern climates develop saccharine elements and high colors, and why the Wisconsin-Minnesota area produces such remarkable waxen and pruinose tints. The influence of the climate is nowhere so easily traced, perhaps, as in the business of seed-growing. Every seedsman knows that certain climates are not only adapted to growth of certain seed crops, but that they exert a profound influence upon the character of the product grown by them. The study of all these inter-relations of climate and plant life falls into three subjects: Phenology, or the study of the periodic phenomena of plants, a subject which loses half its value when considered, as it usually is, without reference to the visible attending features of climate; acclimatization, or a consideration of the means by which plants adapt themselves to climates at first injurious; and secondary variations of plants induced by climate environment.

"The burden of my plea is twofold: First, while not discouraging the instrumental or conventional study of climate, I would encourage its study in terms of plant life. Second, it is essential that the synchronisms of local climate and the phenomena of plants be given the closest attention."

Sedgwick[1] is quite clear as to the direction of the changes; but I cannot see that he makes any actual use of this as a working hypothesis.

"It is a property of living matter to react in a remarkable way to external forces without undergoing destruction. The life-cycle, of which the embryonic and larval periods are a part, consists of the orderly interaction between the organism and its environment. The action of environment produces certain morphological changes in its organism. These changes enable the organism to come into what is practically a new environment, which in its turn produces further structural changes in the organism. These in turn enable, indeed necessitate, the organism to move again into a new environment, and so the process continues until the structural changes are of such a nature that the organism is unable to adapt itself to the environment in which it finds itself. The

[1] *Darwin and Modern Science*, 177 (1909).

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essential condition of success in this process is that the organism should always shift into the environment to which the new structure is suited—any failure in this leading to the impairment of the organism. In most cases the shifting of the environment is a very gradual process (whether consisting in the very slight and gradual alteration in the relation of the embryo as a whole to the egg-shell or uterine wall, or in the relations of its parts to each other, or in the successive phases of adult life), and the morphological changes in connection with each step of it are but slight. But in some cases jumps are made such as we find in the phenomenon known as hatching, birth, and metamorphosis. This property of reacting to the environment without undergoing destruction is, as has been stated, a fundamental property of organisms. It is impossible to conceive of any matter, to which the term living could be applied, being without it. And with this property of reacting to the environment goes the further property of undergoing a change which alters the relation of the organism to the old environment and places it in a new environment."

This quotation is not what we want, because Sedgwick is considering the life-cycle of an individual, which is not our problem at all. It is good as far as it goes, however, and it is the best that I have been able to find.[1]

We get the opposite extreme with Bateson,[2] who says:

"To those who have made no study of heredity it sometimes appears that the question of the effect of conditions in causing variation is one which we should immediately investigate, but a little thought will show that before any critical inquiry into such possibilities can be attempted, a knowledge of the working of heredity under conditions as far as possible uniform must be obtained."

The cap seems to fit and I am quite ready to put it on. Bateson's argument is simply that a change due to reversion might be interpreted as due to a change in environment. This is a possible source of error, but it is one which can be eliminated by making enough experiments and by making experiments with different species of plants. It is hardly conceivable that a reversion to an albino variety, for instance, should coincide with a given change of environment in every experiment and with every kind of plant. On the other hand, it is always a good plan to do the easiest things first, partly because it takes less time to get results, but chiefly because the easy things usually throw light on the hard ones. We know that suitable changes in the environment, if made at a suitable time, will cause such changes in the organism that the next generation differs from the first. It is a very difficult problem to determine the intermediate steps; but it is a relatively simple one to de-

[1] Cf. also Bourne, *Science*, 32, 738 (1910).

[2] *Darwin and Modern Science*, 95 (1909).

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termine what change in the second generation is the result of a change in a single factor of the environment. This is a problem, which has not been attacked by the biologist in any systematic fashion, and it is a problem which will be greatly simplified by an intelligent application of the Theorem of Le Chatelier.

The view of the biologists seems to be that each generation always varies spontaneously from the preceding one to a greater or lesser extent, and that these variations are reproduced more or less completely in the succeeding generation. By the survival of the fittest we eventually get a race which is better adapted to the local conditions than the one from which we started.

The view that I have outlined is that the external conditions tend to produce such changes in the organism that the next generation varies in such a way as to be more adapted to local conditions. By the survival of the fittest and by the continued action of the external conditions, we eventually get a race which is better adapted to the local conditions than the one from which we started.

We reach the same conclusion whichever way we consider the matter. The two views are not mutually exclusive because it is quite possible to consider the variations due to the external conditions as superimposed on the spontaneous variations. If we are to decide between the two points of view, it must be on other grounds than qualitative results. To me, the phrase 'spontaneous variation' seems merely another way of expressing our ignorance. I do not believe in a variation without a cause. If we go back far enough, all variations must be the result of varying external conditions and the real problem is to show what part of any given variation in any given organism is due to the effect of external conditions on the preceding generation and what part is due to the effect of external conditions on still earlier generations. What we study under heredity, as the word is usually used, is the transmitted effect of varying external conditions upon the more or less remote ancestors.

Another objection to the biologist's point of view is that it has not worked out well practically. Being obsessed by the idea of spontaneous variation, he has very rarely taken the trouble to work out carefully the relation between each particular factor of the external conditions and the acquired characteristics of the organism which has become better adapted to its surroundings. If the biologist had had the Theorem of Le Chatelier as a guiding hypothesis, he would not have made this mistake and he would often have done better and more careful work.

I have tried to show that the Theorem of Le Chatelier is a universal law and that it is consequently of great value in enabling us to correlate old facts and to discover new ones.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 59.]

THE ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS BY CENTRIFUGAL ACTION.[1]

BY RICHARD C. TOLMAN.

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1. Work of Previous Investigators and Purpose of this Research.

If the passage of an electric current is associated with the actual transfer of matter along the conductor, a number of phenomena, depending upon the inertia of this matter, are to be expected. The nature of these phenomena was completely discussed by Maxwell; but they have not yet been detected in metallic conductors.[2] In electrolytic conductors, however, the experiments of Hittorf have shown that there is an actual transfer of matter through the solution, accompanying the passage of a current. As an example of the electrical effects which may accompany such a motion of the carriers of electricity or ions, let us consider a solution of si ver nitrate placed in a vertical tube with silver electrodes at the top and bottom. The passage of a current of electricity through this solution from the lower to the upper electrode will be accompanied by a raising of the silver ions in the solution and an approximately equal lowering of the considerably lighter nitrate ions. The net effect produced by the current will be the lifting of a certain weight of material from the lower electrode to the upper; and the work thus done against gravity must correspond to a definite electromotive force which will oppose the passage of the current in this direction.

Effects of this kind were first predicted by Colley,[3] and have also been

[1] This investigation was financially assisted by the American Academy of Arts and Sciences, and a somewhat more extended article describing the research has been published in the *Proceedings of the American Academy of Arts and Sciences*, 46, 110 (1910).

[2] Maxwell, "Treatise on Elec. and Mag.," 3rd edition, Vol. II, 211 *et seq.*; Lodge, "Modern Views of Elec. and Mag.," 3rd edition, 89; Nichols, *Physik. Z.*, 7, 640 (1906).

[3] Colley, *Journal der St. Petersburg chem. und phys. Gesellschaften*, 7, 333 (1875); *Pogg. Ann.*, 157, 370 (1876); *Ibid.*, 157, 624 (1876); *Wied. Beibl.*, 5, 457 (1881); *Wied. Ann.*, 17, 55 (1882).

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considered by various other investigators.[1] Colley himself was able to detect the existence of potential differences between the upper and lower electrodes placed in solutions of silver nitrate and cadmium iodide. The small electromotive forces produced in these solutions by gravity are masked by the presence of much larger variable potential differences which are due to otherwise undetectable differences between the two electrodes used. The effect of gravity is only perceived when a series of measurements is made of the deflections of a very sensitive galvanometer, the positions of the upper and lower electrodes being interchanged between each two measurements by a reversal of the tube containing the electrolyte. The potential differences, which Colley thus found, were of the order of magnitude thoeretically predicted. Later he also showed the presence of a momentary electromotive force produced by the sudden stopping of a falling tube containing cadmium iodide solution.

The experimental problem was next attacked by Des Coudres, who substituted centrifugal force for the weaker action of gravity. He made use of a rotating apparatus in which were placed two tubes with electrodes connected in series, containing cadmium iodide solution. The electrodes were placed 31 cm. and 9 cm. from the center and at 5.8 revolutions per second he obtained an electromotive force of 155 microvolts. Individual measurements, however, varied at times more than 10 per cent. from the mean. Although the substitution of centrifugal force for the force of gravity greatly increases the size of the effect which can be

[1] Lodge, *Phil. Mag.*, **2**, 367 (1876); Hertz, *Wied. Ann.*, **14**, 590 (1881); Des Coudres, *Wied. Ann.*, **49**, 284 (1893); *Ibid.*, **57**, 232 (1896). The electromotive force which is produced in salt solutions by the action of gravity must be carefully distinguished from the actual changes in the concentration of the solute which gravity will produce. The difference in concentration between the solution in the upper and lower ends of a vertical tube, or the central and peripheral portions of a rotating tube can be calculated from simple thermodynamic considerations. It is to be expected, however, that this difference in *concentration* will be very *slowly* established (see Des Coudres, *l. c.*, below). The difference in *potential* between the two ends of the solution is an *immediate* phenomenon which occurs as soon as the tube is set up. It is evident that when the final change in the concentration of a salt solution has completed itself there will no longer be any potential difference between the upper and lower portion of the solution.

A complete bibliography of the theoretical and experimental work which has been done in this field follows: Gay-Lussac, *Ann. chim. phys.*, **11**, 306 (1819); Gouy et Chaperon, *Ann. chim. phys.*, **12**, 384 (1887); Nernst, *Z. physik. Chem.*, **2**, 637 (1888); Duhem, *J. physique*, **7**, 391 (1888); T. v. Turin, *J. russ. Geschichte*, **24**, 90 (1892); *Wied. Beibl.*, **17**, 16 (1893); Des Coudres, *Wied. Ann.*, **49**, 284 (1893); **55**, 213 (1895); Van der Waals, *Z. physik. Chem.*, **5**, 157 (1890); Bredig, *Z. physik. Chem.*, **17**, 459 (1895); Lobry de Bruyn et van Calcar, *Rec. trav. chim.*, **23**, 218 (1904); Franklin and Freudenberger, *Trans. Am. Electrochem. Soc.*, **8**, 29 (1905); Earl of Berkeley and C. V. Burton, *Phil. Mag.*, **17**, 606 (1909); Gibbs, "Scientific Papers," Longmans, Green & Co. (1906), **1**, 144.

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obtained, it is accompanied by the introduction of new errors, produced, for example, by the unequal heating of the central and peripheral portions of the apparatus, as well as by other difficulties. The method was abandoned by Des Coudres in favor of measurements on specially constructed gravity cells. These measurements are of a considerable degree of accuracy, and the results will be given in detail.

As we shall see in the next section, it is possible to derive a relation connecting the electromotive force produced by the action of gravity and the transference number of the electrolyte. The measurements of Des Coudres were made for the purpose of comparing the transference numbers calculated from electromotive force with those determined by the Hittorf method. In his first gravitational experiment he again made use of cadmium iodide solution which, owing to complex ion formation, apparently has a transference number greater than unity, and hence gives a large electromotive force. In the experiment the solution was placed in a glass tube with the electrodes at the two ends about 91 cm. apart. The gravitational electromotive force was deduced from a series of readings of galvanometer deflection, the positions of the upper and lower electrodes being interchanged between each two measurements. The transference number of the solution was found by calculation to be 1.236, differing by at least five per cent. from that determined in the analytical way.

In order to test the theory on more simple solutions, such as the chlorides of the alkali metals, which do not have abnormal values of the transference number, it was necessary to compensate for the decreased size of the effect by the construction of an apparatus with greater difference in height between the electrodes. The electrodes were placed in glass vessels and connected together by a rubber tube full of the solution. The electrode containers could be raised and lowered at will, permitting a difference in level of 377 cm.

The following table gives a summary of his results, including a comparison between the value T_a for the transference number of the anion as calculated from his results and as determined by the Hittorf method. The measurements were made with calomel electrodes (in the case of $CdCl_2$ with Cd amalgam electrodes as well). The e. m. f. is expressed in microvolts per centimeter difference in height:

Salt.	% Conc.	E. m. f.	T_a.	T_a Hittorf.
KCl	16.8	+0.0510	0.50	0.52
NaCl	19.9	—0.0315	0.66	0.65
LiCl	17.3	—0.109	0.77	0.75
HCl	3.56	—0.0218	0.150	0.175
$BaCl_2$	17.0	+0.170	0.64	0.65
$CdCl_2$ (Cal. elect.)	30.1	—0.183	1.10	0.82
$CdCl_2$ (Amalg. elect.)	30.1	—0.221	1.02	

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Des Coudres estimates that the uncertainty in the values of the electromotive forces given is not greater than ± 0.009 microvolt.

In the present investigation a new attempt was made to increase the accuracy of this method of determining transference numbers, by substituting for the effect of gravity the force produced by a centrifugal machine of considerable power. As will be seen in the sequel, the average deviation between successive measurements has in this way been reduced to a very small amount. An estimation of the actual error in the results is, however, somewhat difficult to make.

2. Derivation of an Expression for the Electromotive Force.

In order to derive an expression for the electromotive force produced in an electrolytic solution by the action of gravity, let us consider a vertical tube of height h, filled with the solution and provided with electrodes at the top and bottom. If E is the potential difference in volts between the upper and lower electrodes produced by the action of gravity, then by allowing one faraday of electricity to flow under this electromotive force we could obtain the external work $10^7 EF$ ergs. The passage of this electricity through the solution is accompanied, however, by the transfer of a certain net weight of material from the upper electrode to the lower one. From the principles of energetics, it is evident that this external energy $10^7 EF$ which we could obtain will just be sufficient to restore the solution to its original condition, that is, will do the work of raising the transferred material back from the lower electrode to the upper one. For the sake of definiteness, let us suppose that the electrolyte is a solution of an iodide (C^+I^-) and that we are using iodine electrodes, consisting in practice of platinum electrodes with a small amount of iodine dissolved in the solution. If now, we let one faraday of electricity flow through the solution, we know from the experiments of Faraday and of Hittorf that one atomic weight of iodine or M_I grams will be liberated at the anode or upper electrode and will disappear from the lower electrode, and at the same time that there will be a change in the ratio of salt to water at the two electrodes, such that $T_c M_s$ grams of salt will have apparently been transferred from the anode to the cathode, where T_c is the ordinary or Hittorf transference number of the cation and M_s is the molecular weight of the salt. In order, therefore, to restore the solution to its original condition of uniform concentration, it is necessary to raise $T_c M_s$ grams of salt from the lower electrode to the upper one, at the same time lowering one atomic weight of iodine. If we raise and lower these substances *through* the solution it is evident that they will be buoyed up by force equal to the weight of the volume of solution which they displace. Hence if g is the acceleration due to gravity, and d the density of the solution, the downward forces acting respectively on the salt and the iodine will be $g T_c M_s (1 - v_s d)$ and

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$g M_I(1 - v_{I_2} d)$ where v_s and v_{I_2} are the "partial" specific volumes[1] of the substances. Equating the external electrical work to the work done against these forces in transferring the substance from one electrode to the other, we have the desired relation[2]

$$10^7 EF = hg\,[T_c M_s(1 - v_s d) - M_I(1 - v_{I_2} d)]. \qquad (1)$$

If instead of using a gravity cell we should rotate our solution n times per second, with electrodes at r_1 and r_2, since the centrifugal force acting on one gram at any radius r is $4\pi^2 n^2 r$, the work done in carrying one gram from r_2 to r_1 would evidently be[3]

$$\int_{r_1}^{r_2} 4\pi^2 n^2 r\, dr = 2\pi^2 n^2 (r_2^2 - r_1^2),$$

and our equation for electromotive force becomes

$$10^7 EF = 2\pi^2 n^2 (r_2^2 - r_1^2)\,[T_c M_s(1 - v_s d) - M_I(1 - v_{I_2} d)]. \qquad (2)$$

We see that the value of the electromotive force which is to be measured is proportional to the factor hg or $2\pi^2 n^2 (r^2_2 - r_1^2)$. In the experiments of Des Coudres on gravitational cells, the factor hg was 360,000, while with his rotating apparatus the value of the corresponding factor was 583,000. In the centrifugal experiments which are to be described in this paper the value of the factor was raised to 114,000,000.

The Effect of Hydration.

It has been shown by the careful researches of Buchböck[4] and especially of Washburn[5] that it is possible to distinguish between the ordinary Hittorf transference number and the so-called "true" transference number in which the motion of the ions is referred to a non-electrolytic indicator dissolved in the solution instead of to the water. If water is carried by the current, owing to hydration of the ions, then the two transference numbers will be different

The Hittorf transference number gives, however, the actual number of equivalents of salt which apparently disappear in the neighborhood of one electrode and appear at the other when one faraday of electricity is sent through the solution, and hence the Hittorf transference number gives us the amount of salt which must be moved in order to restore the solution to its original condition of uniform concentration. From a consideration of the method by which the equation for the electromo-

[1] For a definition of "partial" volumes, see Section 8.

[2] In order to derive this equation, any reversible method might be used for restoring the solution to its original condition of uniform concentration. For example the apparent difficulty of moving the substances *through* the solution can be obviated by removing them from the solution with the help of semipermeable membranes. It is easy to show, however, that the relation derived is the same.

[3] It may also be pointed out that the expression $2\pi^2 n^2 (r_2^2 - r_1^2)$ is the increase in kinetic energy when one gram of material is transformed from r_1 to r_2.

[4] Buchböck, *Z. physik. Chem.*, **55**, 563 (1906).

[5] Washburn, *Tech. Quart.*, 21, 164 (1908); THIS JOURNAL, 31, 322 (1909).

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tive force is derived, it is obvious that the *Hittorf* transference number is the one which has been determined in this research.

3. Kinetic Derivation of the Electromotive Force Expression.

In order to derive the equations used in this article, we have considered the production of the electromotive force in a rotating solution from a thermodynamic standpoint. The fact that more work was needed to send a current through a salt solution from the outer to the inner electrodes than in the reverse direction, could be predicted from thermodynamic principles, and the electromotive force, corresponding to this work, could be calculated merely from a knowledge of certain properties of the solution such as transference number and density, which can be experimentally determined. It is also instructive, however, to look at the question from a "kinetic" or molecular point of view. The fact that an electromotive force *is spontaneously* produced by centrifugal force gives us a real knowledge of the internal structure of an electrolytic conductor. It is, indeed, the most striking proof of the existence of free ions in an electrolyte.

Considered from a "kinetic" point of view, a solution of potassium iodide contains free potassium ions and free iodide ions. The iodide ions, however, corresponding to their greater atomic weight, are much denser than the potassium ions, and hence when the solution is rotated they move more readily towards the outer portion of the solution and charge it negatively. In fact from a consideration of the forces acting on the ions in the solution, it is possible to derive the same equation for the electromotive force of a gravity cell as that already obtained from thermodynamic reasoning. The method of proof is similar to that used by Nernst in his consideration of the diffusion cell.

Consider an iodide (C^+I^-) of molecular weight M_s dissociating into the ions C^+ and I^- of atomic weights M_c and M_I. Let v_s be the partial specific volume of the salt in solution and v_c and v_I be the same quantities for the positive and negative ions respectively. Now let us subject a solution of this salt to the action of gravity. If the positive ion C^+ is denser than the iodide ion, it will tend to move downward through the solution more rapidly and will produce a potential gradient in the solution $-dE_1/dh$. As this potential gradient is produced, however, it tends to decrease the downward velocity of the positive ion and increase the velocity of the negative ion so that under the final potential gradient produced they will move downward through the solution with equal velocities. We may now proceed to derive expressions for these equal velocities.

The total downward force acting on one mol. of positive ions is the weight (gM_c), minus the buoyant force exerted by the solution (gM_cv_cd), minus the electrical repulsion ($10^7FdE_1/dh$) corresponding to the poten-

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tial gradient. If u and v are the velocities with which the positive and negative ions move under unit force, the velocity with which they will move under the actual forces can now be calculated by simple multiplication, since the validity of Ohm's law in solutions shows us that the velocity with which the ions move is proportional to the force acting on them.

Equating the velocities of the negative and positive ions, we have[1]

$$u\left(gM_c(1 - v_c d) - 10^7 F\frac{dE_1}{dh}\right) = v\left(gM_I(1 - v_I d) + 10^7 F\frac{dE_1}{dh}\right).$$

Solving for dE_1/dh and integrating between the limits o and h, where h is the difference in height between the electrodes, we have

$$10^7 E_1 F = hg\left[\frac{u}{u+v}M_c(1 - v_c d) - \left(1 - \frac{u}{u+v}\right)M_I(1 - v_I d)\right]. \quad (3)$$

In order to obtain the actual electromotive force between the electrodes, we must consider not only the potential gradient in the solution, but also the potential drops which occur directly at the electrodes due to the electrode reaction $^1/_2 I_2 + (\ominus) = I^-$. Since this reaction is accompanied by the changes in volume $M_I(v_I - v_{I_2})$ and takes place under the difference in pressure between the upper and lower electrodes which is equal to hgd, we must add to the electromotive force E_1, as given in equation (3), the electromotive force E_2 given by the equation below, which is derived by equating the external electrical work to the work produced by the change in volume:

$$10^7 E_2 F = M_I(v_I - v_{I_2})hgd.$$

Noticing that

$$\frac{u}{u+v} = T_c,$$

we obtain

$$10^7(E_1 + E_2)F = hg[T_c M_c(1 - v_c d) + T_c M_I(1 - v_I d) - M_I(1 - v_{I_2} d)]$$

or

$$10^7 EF = hg[T_c M_s(1 - v_s d) - M_I(1 - v_{I_2} d)],$$

which is the same equation we originally obtained by thermodynamic reasoning.

The real interest attached to this kinetic consideration is the almost absolute proof it offers that some degree of dissociation or at least polarization of the salt molecules exists in aqueous solution, since unless the positive and negative components of the salt can move relative to one another we cannot see how a potential gradient is set up by centrif-

[1] It should be noted that when the concentration of the salt in the lower portion of the tube has appreciably increased, the concentration gradient adds new forces tending to slacken the downward motion of the ions. When the final equilibrium is reached the concentration gradient will be such that no potential gradient exists. We are interested, however, in the original condition before appreciable concentration changes have taken place.

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ugal separation. The method gives, of course, no idea of the magnitude of the ionization.

4. Description of Apparatus.

The general arrangement of the rotating apparatus is shown in Fig. 1. It consists of a steam turbin, *A*, with vertical shaft, driving the rotator *B*, which contains the tubes of solution. Electrical connection with the electrodes in the solution was made through the mercury contacts *C*.

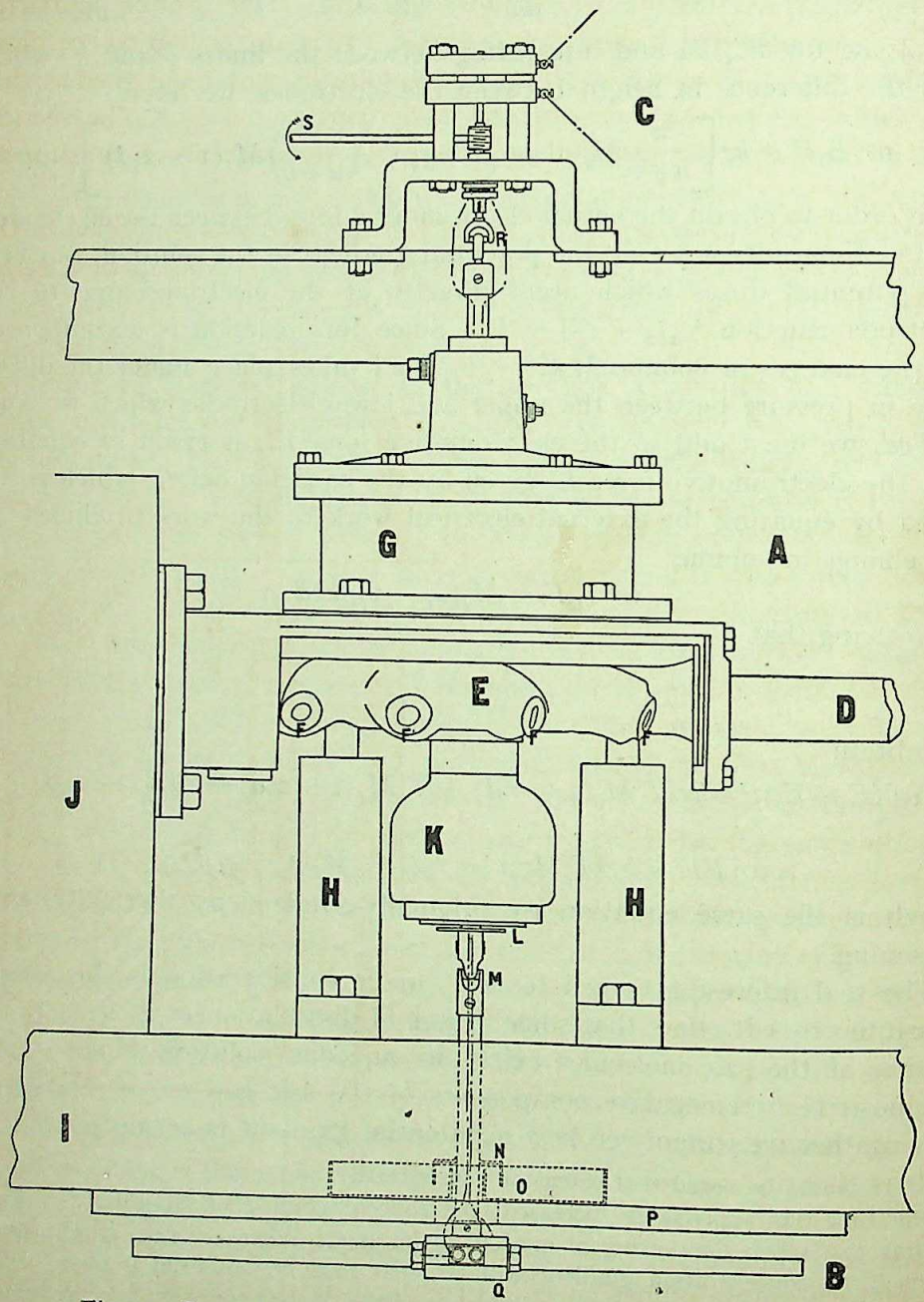


Fig. 1.—General arrangement of the rotating apparatus. 1/8 size.

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a. The Steam Turbin.—The turbin used was a thirty horse-power de Laval loaned for this investigation by the General Electric Co. The turbin wheel was ten inches in diameter. A 2-inch steam pipe, *D*, leads into the annular space *E*, from which the nozzles lead up to the turbin wheel. The holes *F* are opposit the openings to the nozzles and are threaded to receive the bonnets of the nozzle valves (not shown in the drawing). A 3-inch exhaust pipe leads from the exhaust chamber *G*, on the side away from that shown in the drawing. The turbin is supported on the legs *H*, bolted to the cross beams *I*. It is also bolted to the block *J*. Largely for the sake of safety, the apparatus was redesigned with a vertical shaft and was placed in a specially constructed pit. The vertical shaft necessitated the design of some form of thrust bearing to support the rotating system.

b. The Thrust Bearing.—The thrust bearing used was contained in the case *K*, Fig. 1. The details are shown in Fig. 2. It consists of a series of five ball bearings, placed one above the other, so as to distribute the total relative motion which must be cared for. Each ball bearing consists of a series of balls, *F*, in a brass cage, between two hardened steel washers. A shoulder on the shaft *D* rests on the topmost washer *E*, and the lowest bearing rests on the levelling washer *G*, which has a spherical seat. The nut *K* locks the adjustment of the bearing at the proper height. The lateral bearings *A* and *H*, as well as the top bearing of the turbin itself, consist of eminently satisfactory graphite-lined bushings supplied by the Graphite Lubricating Co., Bound Brook, N. J. The lubrication of the ball bearings was also with graphite, which was applied with oil in the form of a paste.

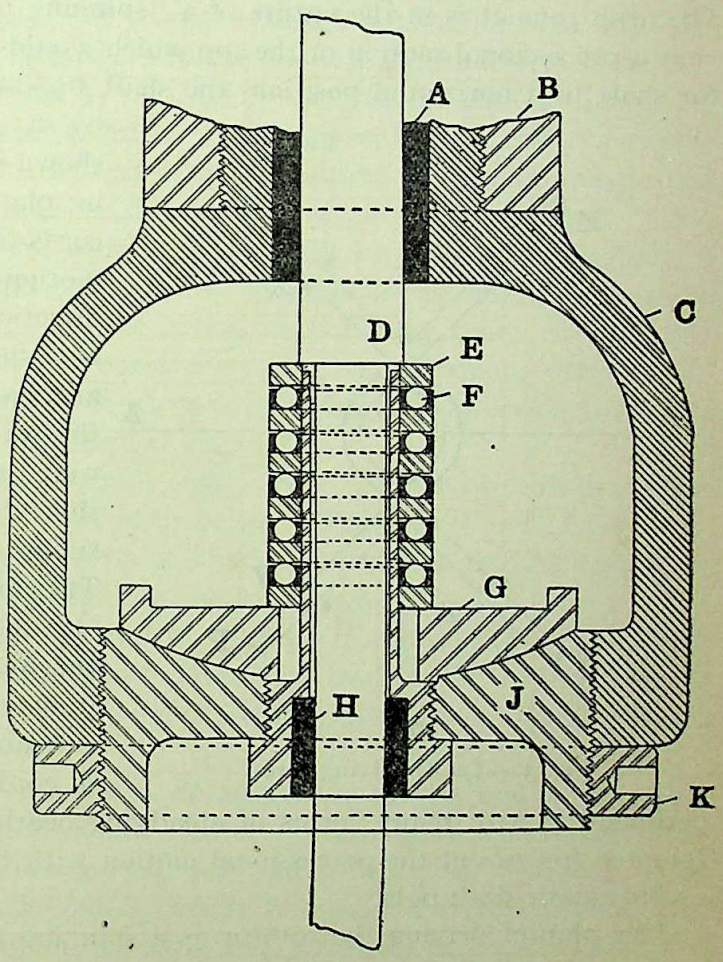


Fig. 2.—The thrust bearing. $^1/_2$ size

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This form of ball bearing was tried only after a number of bearings, including one specially designed for the purpose by The Standard Roller Bearing Co., had failed. The individual ball bearings of which this bearing was constructed were stock $^{13}/_{16}$ inch "ball thrust collar" bearings made by the above firm. The ingenious idea of replacing the series of disks sometimes used in step bearings by a series of ball bearings came in a conversation with Dr. C. A. Kraus, of this laboratory, to whom, in general, I am under the deepest obligation for an intelligent and sympathetic understanding of the many difficulties involved in the construction of an apparatus of this kind.

c. The "Spinning Top."—The rotator *B*, Fig. 1, is two feet in diameter and consists of two hollow steel arms, screwed into a central hub, *Q*. The rotator is hung on a shaft $^{13}/_{16}$ inch in diameter and $8^1/_2$ inches long. This shaft is flexibly connected to the turbin shaft with a Hooke joint, *M*, which permits the rotator to revolve about its own center of gravity. The arrangement is in the nature of a "spinning top." In order to prevent a precessional motion of the top which would quickly raise the rotator shaft to a horizontal position, the shaft was steadied at the point *N* by a system of cords not shown in Fig. 1, but indicated in plan in Fig. 3. The two cords *MN* and *OP* prevent motion of the shaft in the direction *AA*, and two others not shown in the figure are arranged to prevent motion in the direction *BB*. The cords were drawn tight against the shaft through the stationary supports at *W*, *X*, *Y*, and *Z*. The cords were braided cotton $^5/_{32}$ inch in diameter and the wear on them, strange as it may seem, was very inconsiderable. This arrangement of cords was adopted after experimenting with many forms of steadying bearing, in which it was attempted to prevent the precessional motion with rubber washers, springs, or pneumatic dash pots.

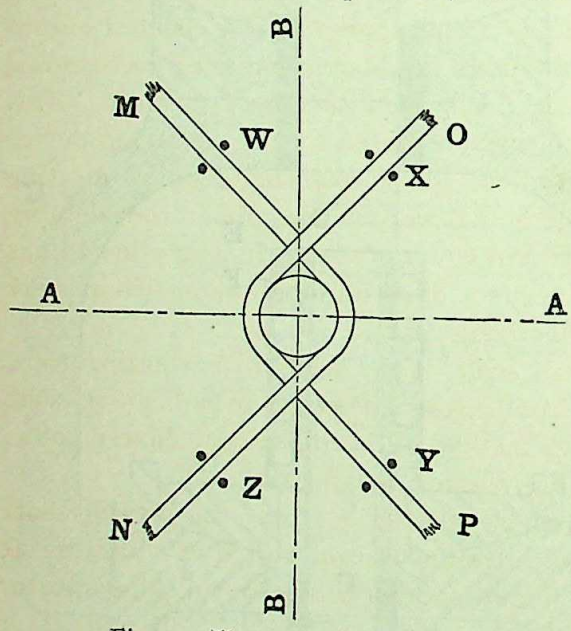


Fig. 3.—The steadying cords.

This plan of driving the rotator as a spinning top must be considered as one of the distinctive features of the apparatus. By this means the rotator was driven up to a speed of 7850 revolutions per minute, giving a rim speed of nearly 50,000 feet per minute. At this speed there

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was a certain amount of vibration of the steadying cords. In general, however, it was found possible to raise the speed at which this vibration took place by moving the supports *W*, *X*, *Y*, and *Z* nearer to the shaft, and there is no doubt that the apparatus could be arranged to go to still higher speeds. As will be seen later, for other reasons, the actual measurements had to be made at speeds of 5000 revolutions or less.

The fact to be specially noticed with regard to this "spinning-top method" is that it permits the driving at a very high speed of a rotator which has not been specially adjusted for either "stationary" or "running" balance. The method was adopted after considerable experimenting with a rotator driven on a shaft with fixed bearings. Although this rotator had been put into "stationary" balance, it caused so great a vibration that one of the bearings gave way at a speed under 2000 revolutions per minute, wrecking a machine upon which a considerable amount of labor had been expended.

The mathematical theory of a symmetrical top rotating with one fixed point and acted upon by gravity alone has been completely developed. It has further been shown by H. Lamb[1] that, in the case of a rotating top hanging below its fixed point, as in this apparatus, the effect of *viscous forces* in the Hooke joint is to produce a gradually increasing precessional motion which would finally raise the axis of the top horizontal. This is the precessional motion which was prevented by the steadying device described above. It must be noticed in general, in designing rotating apparatus of this kind, that the actual motion may differ considerably from that predicted by the dynamical equations since, among other things for example, the latter take no account of restraining forces such as were introduced in this case by the steadying cords.

Some experiments, on a small scale, were made with rotating tops, driven through a Hooke joint from below. There were indications that this would be a most satisfactory method of driving an unbalanced rotor. The whole field is a very profitable one for research.

As a practical detail, it should be pointed out that the rotator shaft must be made short enough not to reach its own period of vibration at the speed employed. It was found impracticable to run this rotator with a shaft 22 inches long.

d. The Rotator.—Fig. 4 gives a detail of one of the two arms which screw into the central hub of the rotator. These arms were made from seamless steel tubing bored out to one-half inch inside diameter. The peripheral end of the tube was closed by screwing in a plug of steel, the threads of which were figured to withstand the shear at 8000 revolutions per minute, produced by the combined outward action of the centrifugal force of the plug and that of the contents of the tube, assuming them to

[1] H. Lamb, *Proc. Roy. Soc., London*, 80, *A*, 168 (1908).

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be a liquid of specific gravity 1.3. In order to prevent leakage of liquid through the screw threads, the plug was silver-soldered in position.

The thickness of wall at the peripheral end of the tube was enough to prevent bursting as calculated by Clavarino's formula for thick hollow cylinders. This thickness of wall was also great enough to sustain the

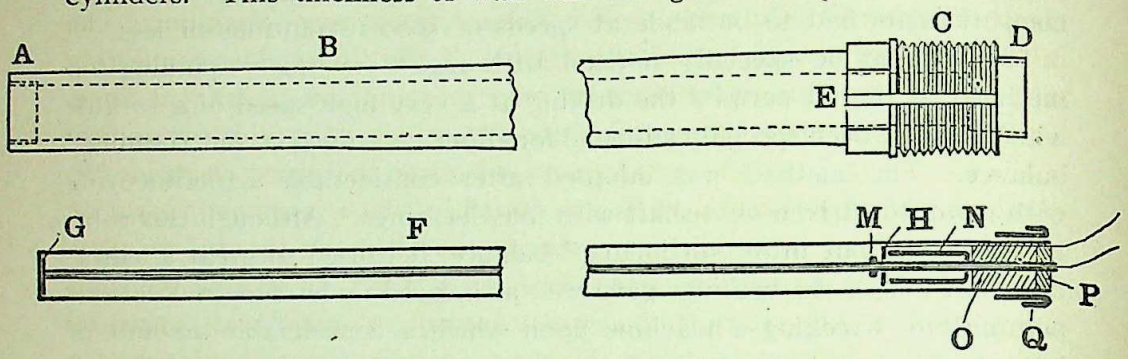


Fig. 4.—Rotator arm and solution tube. $^1/_2$ size.

outward tension as far as the point *B*, 3 inches from the end of the tube. From this point on towards the center the tube had to gradually increase in diameter in order to sustain the constantly increasing load. If r is the radius at any point where the section is s, D the density, f the tensil strength of the material, and n the number of revolutions, evidently $fds = 4\pi^2n^2rDsdr$. Integrating this equation and solving, the proper dimensions for the inner end of the arm were found. The screw thread on the inner end of the arm was sufficient to prevent the arm from shearing out from the hub.

e. The Solution Tube.—The solutions experimented on were iodides with iodine electrodes. The actual tubes which contained the solutions were made of glass. This was the only material found which was an insulator and at the same time was not attacked by the iodine. The latter condition was of great importance since the slightest loss of iodine in the neighborhood of either of the electrodes created a large potential difference between them. The tubes were carefully annealed and were floated in oil inside the rotator arms; nevertheless, the end thrust produced by the centrifugal force was great enough to break many tubes even at speeds as low as five thousand revolutions per minute.

With the hope of obtaining some material which would stand higher speeds, a great many other materials for tubes were investigated, including porcelain, paraffined paper and wood, celluloid, vulcanite, and steel tubes lined with paraffin, sulfur, and enamel, but none was found satisfactory. Tubes of vulcanite, which has a specific gravity only slightly greater than water, practically floated in the steel arm without danger of breakage, and many experiments were made with them. There seemed, however, to be a distribution of iodine between the hard rubber and the solution which made it very difficult to keep the iodine concen-

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tration the same at the two electrodes, and they were finally discarded in favor of glass.

Fig. 4 gives a detail of one of the tubes with its electrodes. The tubes were annealed by carefully wrapping them in asbestos and heating in a large electric furnace to about 500° and then allowing the furnace to cool, which took a day and a half. The electrodes were platinum. The outside electrode *G* rested on the bottom of the tube. The connecting wire had to be platinum-iridium in order to stand the centrifugal force. This wire was insulated from the solution by a glass tube which is slightly enlarged at *M*. On the enlargement *M* rests the inner electrode *H*. *N* shows the cross section of a glass thimble which is slipped down on to the electrode. A bubble of air was entrained in this thimble to allow for temperature expansion, and to provide a means of stirring the solution. Melted ceresin which had been specially purified was poured on top of the thimble at *O* and this was covered with a thin layer of a molten cement, *P*, which consisted of a mixture of wood tar and shellac.[1]

The tube is made to slip into the rotator arm and rests at the outside end on a disk of rubber packing. It is surrounded by oil to equalize the hydrostatic pressure. A short piece of rubber tubing is slipped onto the glass tube and turned back on itself as shown in the figure at *Q*. The tube projects from the end of the arm far enough so that the turned-back rubber just meets the end of the arm at *D*, and a piece of "bill-tie" tubing is slipped over the rubber tubing and the arm to prevent leakage of oil.

The leads from the electrodes come out from the rotator in the grooves *E* and are covered with small rubber tubing. Ordinary optical tubing was not a good enough insulator, but insulation was used which was stripped from 22-gage rubber-covered wire supplied by the Simplex Electrical Co., of Cambridgeport. The wires were attached to binding posts on the rotator hub, from which electrical connection was carried up to the mercury contacts.

f. The Electrical Connections.—The path taken by the electrical connections is indicated by dot and dash lines in Fig. 1. Leads from the binding posts on the rotator hub pass up through the center of the hollow rotator and turbin shafts and make connection with the mercury contacts. The wire used was 22-gage rubber-covered, as ordinary insulation would not stand the severe conditions of temperature and the effect of moisture.

At *L*, in Fig. 1, is a brass disk about 2.5 inches in diameter fastened to the rotating shaft. This disk prevents any leakage of water from the turbin trickling down the Hooke joint and getting into the hollow rota-

[1] This useful cement was discovered by Dr. C. A. Kraus and Mr. R. D. Mailey, of this laboratory.

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tor shaft and thus interfering with the insulation. *O* is a stationary pan about 10 inches in diameter with a central hole for the shaft to pass through. This pan catches accidental dripping from the turbin and protects the hub of the rotator and its binding posts. Further protection is provided by a copper disk, *N*, with turned-down edges. This disk rotates with the shaft and covers the central hole in the pan *O*. The disk also radiated the heat from the turbin and from the friction of the steadying cords, which otherwise traveled down the shaft and produced bad temperature differences between the central and peripheral electrodes.

g. *The Mercury Contacts.*—Connection between the leads, which came up through the hollow shafts, and the external measuring circuit was made through the mercury contacts *C* indicated in Fig. 1 and shown in detail in Fig. 5. The leads from the electrodes were made fast to the binding posts *M* and *N*, and e ectric connection was made through the

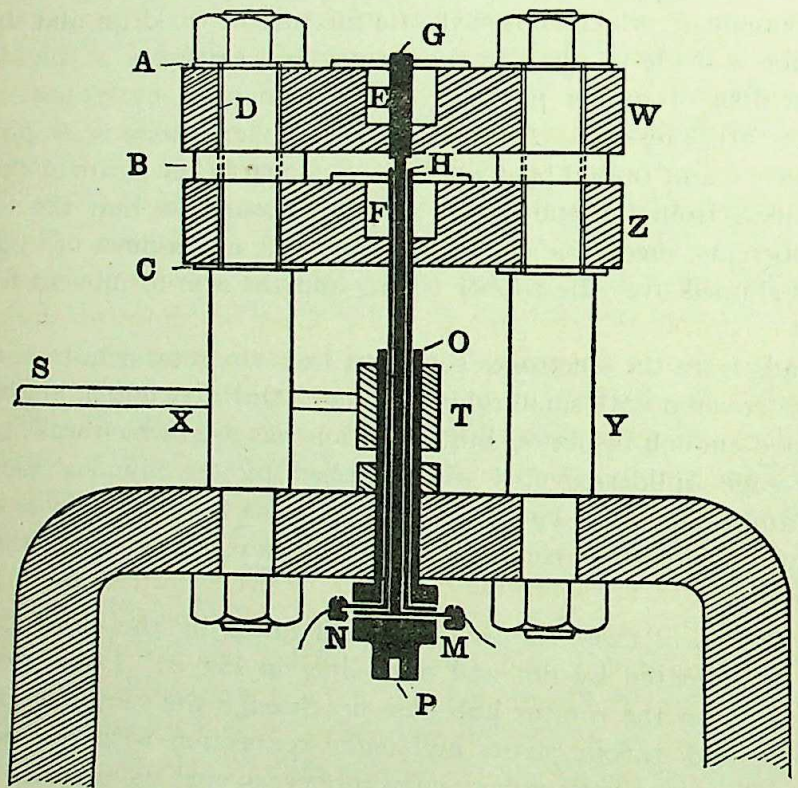


Fig. 5.—The mercury contacts. $^1/_2$ size.

small rotating shafts *G* and *H* with mercury, which was placed in the circular troughs *E* and *F* in the steel blocks *W* and *Z*. The two small shafts are insulated from one another and from the outside driving shaft *O* by fine rubber tubing, and at the bottom by vulcanite disks. The steel blocks are insulated from each other and their supports *X* and *Y*

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by vulcanite washers and sleeves. Connection is made from the steel blocks to the measuring instruments.

The apparatus was specially designed with the purpose of eliminating the production of electromotive forces at the point of contact between the moving and stationary parts. For this reason the shafts were made as small as possible, $^3/_{16}$ inch in diameter, thus reducing the relative velocity at the point of contact; mercury was chosen as the contact substance, and the whole apparatus was made of the same material, steel, throughout. Measurements of the electromotive forces occurring in these mercury contacts were made by driving the apparatus with the contacts short-circuited. The potential differences found were in the neighborhood of $^1/_{20}$ millivolt.

h. The Magneto.—Returning again to Fig. 5, *T* is a worm driving the shaft *S* through a worm wheel not seen in the drawing. Measurements of the speed of rotation of the apparatus were made by reading the voltage produced by a magneto driven from this shaft *S*. This was a small three-bar magneto manufactured a number of years ago by the Holtzer Carbot Co., of Brookline. This was the least satisfactory part of the apparatus, since the voltage readings at a constant speed were liable to small, sudden fluctuations largely due to poor contact at the commutator. Both graphite and woven wire commutator brushes were tried. The accuracy of the speed determinations, however, seemed to be of the same order of magnitude as that of the other measurements, and it did not seem advisable to procure one of the newer magnetos or any of the more costly forms of apparatus for speed measurement. A small motor was arranged for driving the magneto independently, and the magneto was standardized after each series of measurements with the help of a stop-watch and suitable counter.

i. The Electrical Measuring Instruments.—The potential differences obtained were of the order of a few millivolts. For their measurements a Leeds and Northrup potentiometer and a suitable galvanometer were used. A cadmium element supplied by the Weston Electric Co. was used as a standard cell, and this was further compared with another Weston cell both at the beginning and end of the measurements. In the actual experiments a reading of the voltmeter, which gave the speed of the apparatus, and the potentiometer reading were taken as nearly simultaneously as possible.

5. The Method of Procedure.

With the apparatus described, measurements were made on solutions of potassium, sodium, lithium, and hydrogen iodides. The solutions contained exactly 1 mol of the salt and $^1/_{100}$ mol of I_2 in a kilogram of water. In the case of hydrogen iodide, owing to the oxidation of the acid, there was a gradual increase in the amount of I_2 present in the solution.

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A rough colorimetric analysis of the solution as finally used showed the presence of about $^2/_{100}$ mol I_2 per kilogram of water.

The glass tubes whi h contained the rotating solutions have already been described. In the experiments as finally performed only one tube was used, an approximate counterbalance being placed in the other arm of the rotator. By connecting two tubes in series, it would have been possible to double the electromotive force to be measured. This would not have greatly increased the certainty of the measurements, however, since, on stopping the rotator, the residual potential differences between the two electrodes were always found to be in the same direction, and by connecting two tubes in series the size of the error as well as that of the potential difference to be measured would have been increased.

Before filling the tubes, they were carefully rinsed with some of the solution to be used. The electrodes were heated to incandescence in a blast lamp and placed in the solution without being touched by the fingers.[1] By using care, it is possible in this way to reduce the original electromotive force between the two electrodes to the neighborhood of 0.2 millivolt or less. The small variable electromotive forces which do persist are probably partly due to differences in temperature between the two ends of the solution. As already described, the tubes were sealed with purified ceresin. This was almost the only material found whose presence near one of the electrodes did not produce a large electromotive force.

After the apparatus had been set up ready for rotation it was tested for insulation. This is very important, since any leakage between the leads coming from the solution would apparently have decreased the size of the electromotive force produced. This test was carried out by disconnecting one of the leads from its binding post on the hub of the rotator and applying a drop of 1.5 volts at the other end of the leads where they joined the measuring system. A galvanometer was in series with the potential drop to measure the current leaking from one lead to the other.[2]

In general, for the final experiments the galvanometer was absolutely stationary, and if there was more than a trace of a deflection, the trouble was eliminated before making a run. A deflection of one millimeter on the galvanometer scale would have corresponded to a resistance of about 1.5×10^9 ohms between the leads.

In the experiments a number of readings of the residual electromotive force were taken with the rotator stationary. It was then brought up to speed and a new series of readings commenced as soon as possible.

[1] Laurie, *Z. physik. Chem.*, 64, 617 (1908).

[2] In order to make the test more thorough, the lead which had been disconnected from the binding post was connected to the steel rotator. Until considerable experience had been gained, it was very difficult to eliminate leaks between the wires coming from the electrodes and the rotator.

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After running for several minutes, the steam was shut off and more readings of the residual electromotive force commenced as soon as the rotator had stopped. The voltmeter attached to the magneto was placed near the potentiometer so that a determination of the speed of the apparatus was made immediately after each measurement. The approximate time when each measurement was taken was also recorded.

At the end of a day's measurements, the magneto was standardized with a stop-watch and counter. Usually about half a dozen standardizing runs were made at speeds in the neighborhood of those used in the actual measurements. Each run lasted about a minute. The stop-watch was started when some even figure appeared on the counter, and stopped similarly about a minute later. In general, five readings of the voltmeter were made, one before the stop-watch was started, the next three at intervals of fifteen seconds, and the last one after the watch had been stopped. It was not easy to hold the speeds constant enough to make standardizing runs of over a minute desirable.

6. The Experimental Results.

In the following tables are given the data on which the calculations for each of the salts investigated are based. The first column gives the time when the observation was taken, the second column the reading of the voltmeter, V (in decivolts), which indicated the speed of the apparatus, and the third column the potential difference in millivolts, $E \times 10^3$, this being called negative when in the opposit direction from that produced by the centrifugal force. The radii of the two electrodes, r_2 and r_1, are also given, and the data for the standardization of the magneto. In the case of all salts investigated, the inside electrode was positive with respect to the outside one during rotation.

It is a striking fact that upon stopping the rotator the residual electromotive force is always found to be in the opposit direction from that produced by the centrifugal force. It will also be seen from an examination of the data that there is a general tendency for this residual electromotive force to increase somewhat in magnitude and then in the course of a few minutes gradually to disappear. The average magnitude reached by this residual electromotive force is 0.2 to 0.3 millivolt.

At first sight, it might seem possible to explain this residual potential difference by assuming that the outer electrode was heated more by the friction of the air, during rotation, than the inner one, since, as a matter of fact, a difference in temperature of 1° would have produced a residual electromotive force of about 0.25 millivolt in the direction actually found.[1]

[1] In order to determin the value of the electromotive forces produced by temperature differences between the electrodes, the thermoelectric power was carefully measured for a number of different circuits of the type—platinum ⟶ salt solution: salt solution ⟶ platinum. The writer hopes to present the results of measurements of this kind in a later paper.

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This explanation, however, would not account for the fact that the residual electromotive force tends to increase after the machine had been stopped, and the very conditions removed which were supposed to create the temperature difference.[1] This increase in the magnitude of the residual electromotive force after stopping the machine was much easier to follow and the final value reached was much larger, in some earlier experiments where *vulcanite* tubes were used instead of glass for containing the solution.[2] This might indicate that the gradual increase of electromotive force after stopping the rotation is due to the gradual emergence into the solution of some constituent which had been forced into the pores of the tube by the centrifugal force or the pressure. Whatever the true explanation, the phenomenon is so complicated that it seemed best not to hazard a guess as to the probable size of the residual electromotive force *during* rotation and no correction was made for it in the calculations.

Further development of the centrifugal method should be in the direction of eliminating these residual potential differences between the electrodes. This could best be done by having the liquid circulate through the apparatus so as to pass from one electrode to the other and thus assure the same conditions at both.

7. Ratio of the Electromotive Force to the Square of the Number of Revolutions Per Second.

From equation (2) it is evident that the electromotive force produced by the rotation should increase as the square of the number of revolutions per second, that is, E/n^2 for a given solution should be a constant. The degree of the constancy of this quantity is illustrated by the fifth column in Tables I–IV, which gives the values of E/n^2 as calculated from the data. Considering the separate runs in a series of measure-

[1] Attempts were made to actually measure the temperature difference between the two electrodes, by placing in the tube an ordinary thermoelectric circuit with iron-nickel junctions at the outer and inner ends. Connection between this thermoelectric circuit and the measuring instruments was made through the mercury contacts already described. It was found, however, that the small electromotive forces arising in these mercury contacts were large enough to obscure those produced by the iron-nickel junctions, and the method was abandoned. There seems to be no practical metallic junction of higher thermoelectric power than the iron-nickel combination.

In some earlier experiments very definit temperature effects were produced by heat which traveled down the rotator shaft. These effects were eliminated, however, by the copper radiating disk N, Fig. 1, already described, see p. 134.

[2] In these experiments made with vulcanite tubes, there was also the difference that the rotator was driven in a closed case instead of in the open air. Since the air in the case was considerably heated by the rotation, larger temperature differences might have been expected between the two electrodes. Nevertheless, this would not account at all for the increase in residual electromotive force after the rotator had been brought to rest.

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TABLE I.

(Dec. 2, 1909.)

Solution: Molal KI, $^1/_{100}$ Molal I_2. $r_2 = 29.40$ cm., $r_1 = 4.3$ cm.

Standardization of magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 1.050$ (7 exp. av. dev. ±0.0145).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 1.050$ = rev. per sec.	$E/n^5 \times 10^6$.	Dev. from mean.
10.54	0	—0.30	....	...	....
11.12	0	—0.10	....	...	....
.23	0	—0.50	....	...	....
.25	0	—0.55	....	...	....
.28	60.0	+2.58	62.9	652	— 5
.29	58.5	2.47	61.4	655	— 2
.30	59.0	2.52	61.9	658	+ 1
.30$^1/_2$	59.8	2.55	62.8	647	—10
.31$^1/_2$	0	—0.15	....	...	....
.32	0	—0.30	....	...	....
.34	0	—0.18	....	...	....
.36	0	—0.14	....	...	....
.40	0	—0.17	....	...	....
.41$^1/_2$	71.5	+3.65	75.0	649	— 8
.42	71.2	3.73	74.7	668	—11
.43$^1/_2$	72.0	3.73	75.5	655	— 2
.44	72.7	3.90	76.2	672	+15
.45	73.1	3.93	76.7	668	+11
.46	0	—0.25	....	...	....
.47	0	—0.18	....	...	....
.49	0	+0.05	....	...	....
.50$^1/_2$	0	0.17	....	...	....
.52$^1/_2$	0	0.25	....	...	....
.55	78.0	4.38	81.9	653	— 4
.55$^1/_2$	77.5	4.35	81.3	658	+ 1
.56	77.0	4.25	80.8	651	— 6
.57	....	4.25	....	...	....
				Average, 657.1	±6.3

ments, we see a tendency for the individual measurements of the *first* run to show the largest deviations from the mean. There is probably some connection between this and the fact that the value reached by the residual electromotive force is also largest after the first run in a series. In many of the individual runs there is a tendency for the electromotive force to decrease somewhat during the run. This would correspond to the gradual production of a negative residual electromotive force. As already pointed out, the nature of these residual potential differences is too uncertain to permit of a trustworthy correction.

8. The Partial Volumes of Iodine and the Iodides.

Before making a calculation of the transference numbers from the electromotive force data which we have just considered, a knowledge

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TABLE II.

(Dec. 23, 1909.)

Solution: Molal NaI, $^1/_{100}$ molal I_2. $r_2 = 29.45$ cm., $r_1 = 4.2$ cm.

Standardization of Magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 0.8695$ (8 exp. av. dev. ± 0.0035).

Time.	V = Voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8695$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
10.12	0	—0.16	....	...	....
.15	0	—0.04	....	...	....
.22	0	—0.35	....	...	....
.25 1/2	66.2	+3.00	57.6	904	+15
.26 1/2	65.9	2.95	57.3	898	+ 9
.27	65.9	2.83	57.3	862	—27
.28	65.9	2.83	57.3	862	—27
.28 1/2	66.2	2.92	57.6	880	— 9
.30	0	—0.24	....	...	....
.30 1/2	0	—0.28	....	...	....
.31 1/4	0	—0.17	....	...	....
.32 1/2	0	0.00	....	...	....
.35	73.2	+3.61	63.7	889	0
.35 1/2	74.2	3.70	64.5	889	0
.36 1/2	74.8	3.75	65.1	885	— 4
.37	75.1	3.79	65.3	888	— 1
.38	76.0	3.88	66.1	887	— 2
.39 1/2	0	—0.26	....	...	....
.40	0	—0.26	....	...	....
.41	0	—0.17	....	...	....
.42	0	—0.07	....	...	....
.43 1/2	0	—0.00	....	...	....
.45	0	+0.03	....	...	....
.46	0	0.05	....	...	....
.48 1/2	74.5	3.70	64.8	881	— 8
.49	74.2	3.72	64.5	893	+ 4
.50	74.8	3.72	65.1	877	—12
.50 1/2	74.5	3.71	64.8	883	— 6
.51	74.5	3.70	64.8	881	— 8
.52	74.0	3.66	64.4	882	— 7
.53 1/2	0	—0.15	....	...	....
.54 1/2	0	—0.10	....	...	....
.55 1/2	0	—0.06	....	...	....
.57	0	—0.05	....	...	....
.58 1/2	0	—0.06	....	...	....
.60 1/2	0	—0.10	....	...	....
11.03	80.0	+4.37	69.5	905	+16
.03 1/2	81.2	4.53	70.6	910	+21
.04 1/2	82.8	4.60	72.0	888	— 1
.05	83.2	4.65	72.3	889	0
.06	84.0	4.77	73.0	895	+ 6
.06 1/2	84.1	4.80	73.1	899	+10
.07 1/2	0	—0.23	....	...	....
.08	0	—0.23	....	...	....

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Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8695$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
.10	0	—0.04	....	...	....
.11 1/2	0	+0.12	....	...	....
.14	0	0.17	....	...	....
.16	0	0.17	....	...	....
.18 1/2	74.1	3.73	64.5	897	+ 8
.19 1/4	75.0	3.85	65.2	905	+16
.20	74.8	3.76	65.1	887	— 2
.20 3/4	74.2	3.73	64.5	896	+ 7
.21 1/2	73.9	3.68	64.2	892	+ 3
.22 1/2	0	—0.24	....	...	....
.23 1/2	0	—0.18	....	...	....
.28	0	+0.18	....	...	....
				Average, 889.0	±8.5

TABLE III.

(Dec. 10, 1909.)

Solution: Molal LiI, $^1/_{100}$ molal I_2. $r^2 = 29.45$ cm., $r_1 = 4.2$ cm.

Standardization of Magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 0.8605$ (6 exp. av. dev. ±0.0040).

Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8605$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
10.10	0	—0.2	....	....	....
.24	0	—0.20	....	....	....
.29	0	—0.15	....	....	....
.33	0	—0.30	....	....	....
.36	59.2	+3.25	50.9	1253	+70
.36 1/2	60.2	3.26	51.8	1217	+34
.37	61.2	3.30	52.6	1192	+ 9
.37 1/2	61.5	3.30	52.9	1179	— 4
.38 1/4	61.9	3.31	53.3	1163	—20
.39	0	—0.20	....	....	....
.40	0	—0.5	....	....	....
.41 1/2	0	—0.4	....	....	....
.44	0	—0.13	....	....	....
.45 1/2	64.1	+3.65	55.1	1202	+19
.46	64.8	3.72	55.8	1193	+10
.46 1/2	65.1	3.68	56.0	1172	—11
.47 1/2	66.0	3.76	56.8	1165	—18
.48	66.3	3.77	57.1	1137	—26
.49	0	—0.15	....	....	....
.49 1/2	0	—0.2	....	....	....
.50	0	—0.25	....	....	....
.51	0	—0.25	....	....	....
.51 1/2	0	—0.25	....	....	....
.53	0	—0.22	....	....	....
.56	0	—0.25	....	....	....
.58 1/2	69.5	+4.23	59.8	1182	— 1
.59	69.3	4.22	59.6	1188	+ 5
.60	69.2	4.18	59.5	1180	— 3
11.00 1/2	68.7	4.13	59.1	1183	0

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Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 0.8605$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
.01	68.4	4.05	58.8	1171	—12
.01 3/4	68.3	4.04	58.75	1170	—13
.02 3/4	0	—0.14	....	....	....
.03 1/4	0	—0.18	....	....	....
.04	0	—0.14	....	....	....
.05 1/2	0	+0.10	....	....	....
.07 1/2	0	0.15	....	....	....
.09 1/2	0	0.16	....	....	....
.11	0	0.09	....	....	....
.13	73.8	4.80	63.5	1190	+ 7
.13 1/4	74.0	4.80	63.7	1182	— 1
.14	74.0	4.75	63.7	1169	— 4
.14 1/2	74.1	4.77	63.75	1173	—10
.15 1/2	74.5	4.84	64.1	1178	— 5
.16	74.8	4.85	64.4	1170	—13
.17	0	—0.19	....	....	....
.17 1/2	0	—0.27	....	....	....
18	0	—0.30	....	....	....
.19	0	—0.30	....	....	....
.20 1/2	0	—0.28	....	....	....
.24	0	—0.32	....	....	....
.39	0	—0.36	....	....	....
...	....	....	....	....	....
...	....	....	....	....	....
...	....	....	....	....	....
.44	0	—0.20	....	....	....
.46	0	—0.03	....	....	....
.48	80.1	+5.62	68.9	1184	+ 1
.48 1/2	79.8	5.61	68.7	1189	+ 6
.49	79.3	5.48	68.25	1177	— 6
.49 1/2	79.1	5.47	68.1	1179	— 4
.50 1/2	78.5	5.38	67.5	1180	— 3
.52	0	—0.16	....	....	....
.52 1/2	0	—0.25	—..	....	....
.53 1/2	0	—0.30	....	....	....
.55	0	—0.25	....	....	....
.56 1/2	0	—0.25	....	....	....
.58	0	—0.25	....	....	....
12.00	84.1	+6.30	72.4	1202	+19
.00 1/2	84.5	6.33	72.7	1198	+15
.01	84.1	6.18	72.4	1180	— 3
.02	84.0	6.15	72.25	1178	— 5
.02 1/2	84.1	6.16	72.4	1175	— 8
.03	0	—0.18	....	....	....
.04	0	—0.35	....	....	....
.04 1/2	0	—0.35	....	....	....
.05 1/2	0	—0.25	....	....	....
.06 3/4	0	—0.07	....	....	....
.09 1/2	0	+0.15	....	....	....
			Average,	1183	±11.7

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TABLE IV.

(Nov. 20, 1909.)

Solution: Molal HI, approx. M/50 I_2. $r_2 = 29.43$ cm., $r_1 = 4.51$ cm.

Standardization of Magneto: $\frac{\text{Rev. of rotator per second}}{\text{Voltage of magneto}} = 1.0125$ (6 exp. av. dev. ±0.0095).

Time.	V = voltage of magneto.	$E \times 10^3$ = E. M. F.	$n = V \times 1.0125$ = rev. per sec.	$E/n^2 \times 10^6$.	Dev. from mean.
10.53	0	—0.38	....	....	....
11.10	0	—0.45	....	....	....
.17	0	+0.50	....	....	....
.18½	63.0	1.55	63.8	380	+ 4
.19½	70.0	1.83	70.8	365	—11
.20	70.2	1.90	71.0	377	+ 1
.20½	70.0	1.90	70.8	379	+ 3
.21½	0	—0.17	....	....	....
.22½	0	—0.25	....	....	....
.24	0	—0.22	....	....	....
.25	0	—0.15	....	....	....
.26	0	—0.1	....	....	....
.28	0	—0.08	....	....	....
.29½	73.5	+2.13	74.4	385	+ 9
.30½	76.0	2.17	76.9	367	— 9
.30	76.1	2.25	77.0	379	+ 3
.31½	75.5	2.25	76.4	385	+ 9
.32	75.8	2.25	76.7	382	+ 6
.33	0	—0.12	....	....	....
.33½	0	—0.20	....	....	....
.35	0	—0.16	....	....	....
.36½	0	—0.12	....	....	....
.38(?)	0	—0.01	....	....	....
.45	78.5	+2.35	79.4	373	—3
.46	79.0	2.33	79.9	365	—11
.46½	78.5	2.40	79.4	381	+ 5
.47	78.2	2.35	79.1	376	0
.48	0	—0.10	....	....	....
.48½	0	—0.15	....	....	....
.49½	0	—0.15	....	....	....
.50½	0	—0.10	....	....	....
.52	0	—0.07	....	....	....
.53	0	—0.02	....	....	....
.54½	79.0	+2.45	79.9	384	+ 8
.55	80.5	2.45	81.4	370	— 6
.56	81.0	2.45	81.9	366	—10
.57	0	—0.10	....	....	....
.57½	0	—0.15	....	....	....
.58	0	—0.15	....	....	....
.60	0	—0.07	....	....	....
12.03	0	+0.06	....	....	....
			Average,	375.9	±6.1

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of the partial volumes of iodine in iodide solutions and of the iodides in aqueous solution is necessary.

The partial specific volume of any constituent of a solution may be defined as the increase in volume of the solution when one gram of the constituent in question is added to a quantity of the solution so large that the addition causes no appreciable change in concentration. In the language of mathematics, if the addition of Δm grams of the constituent at the concentration under consideration produces an increase of Δv cc. in the volume of the solution, the partial volume of the substance may be defined as the limit approached by $\Delta v/\Delta m$ as Δm approaches zero.

The quantity $\Delta v/\Delta m$ and its limit the partial volume dv/dm may be obtained by the same experimental methods used for the determination of the specific gravity of solutions, or, indeed, may be calculated from specific gravity data if such are available.

In the author's more complete article,[1] a method is presented of calculating partial volumes from specific gravity data, and calculations are made from existing data of the partial volumes of the salts used. Determinations which were made of the partial volume of iodine are also described. The values used in calculating the transference number are given in the table in the next section.

9. Calculation of the Transference Number.

Substituting for π its value, and for F the value 96580, equation (2) may be written:

$$T_c = \left(\frac{4.895 \times 10^{10}}{(r_2^2 - r_1^2)} \frac{E}{n^2} + M_1(1 - v_{I_2}d)\right) \div M_s(1 - v_s d).$$

Using the average values of E/n^2 the transference number of the cation T_c was calculated for each of the salts. The data and results are given below:[2]

Solution.	$E/n^2 \times 10^6$.	$(r_2^2-r_1^2)$.	M_s.	v_s.	M_I.	v_{I_2}.	d.	T_c.	P. E.
$M/1$ *KI*, $M/100$ I_2....	657.1	846.0	166.0	0.284	126.9	0.2376	1.115	0.486	±0.001
$M/1$ *NaI*, $M/100$ I_2...	889.0	849.3	149.9	0.244	126.9	0.2376	1.110	0.385	±0.001
$M/1$ *LiI*, $M/100$ I_2...	1183	849.3	133.9	0.2605	126.9	0.2376	1.096	0.268	±0.0013
$M/1$ *HI*, $M/50$ I_2....	375.9	846.2	127.9	0.282	126.9	0.2376	1.090	0.816	±0.001

a. The Accuracy of the Results.—The last column in the table gives the extremely small "probable error" introduced into the value of the transference number, by the deviations between the different measurements of E/n^2. It was obtained by dividing the mean deviations by the square root of the number of observations. It is not a satisfactory measure

[1] *Proc. Amer. Acad. Arts Sci.*, 46, 109–146 (1910).

[2] The values of E/n^2 are, of course, all negative since the current tends to flow from the outer to the inner electrode.

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of the reliability of the transference numbers, since there is considerable probability that the "residual" electromotive force existing between the electrodes during rotation were more likely to be in one direction than the other. The value ±0.010 may be taken as a fairer measure of the probable accuracy of the determinations. In the case of KI, this would correspond to an average error of about 0.1 millivolt in the electromotive force.

b. The Effect of Pressure on the Results.—In deriving the equation in Section 2 for the potential difference of a cell under the influence of centrifugal force, the tacit assumption was made that the quantities v_s, v_{I_2} and d are, throughout the solution, the same as those calculated from density measurements made at atmospheric pressure. This is not strictly true, since there is considerable pressure produced in the solution by the centrifugal force.

In the author's original article[1] an exact equation is derived in which the variation of these quantities with the pressure is allowed for; and it is shown that the error introduced by neglecting the variation is, as would be expected, entirely negligible.

In considering the pressure gradient in the tube, it must also be pointed out that the transference number determined in these experiments is the transference number which exists when the solution is actually under the influence of that particular pressure gradient. Owing to their enormous "internal pressure" the properties of liquids are, however, in general but little affected by changes in the external pressure.

c. The Effect of Dissolved Iodine on the Results.—In the case of the alkali iodides one per cent. of the $\bar{I}$ ion was changed into $\bar{I}_3$ ion by the iodine present. In the HI solution, owing to oxidation, about twice as much iodine was present. The transference number would, however, be only slightly affected by the small admixture of $\bar{I}_3$ ion.[2]

10. Comparison of the Results with Other Transference Measurements.

The available data on the transference numbers of iodides are very few, and, of these, many are vitiated by the use of membranes in the apparatus.[3] The most satisfactory data for comparison are the values determined by Washburn[4] for the Hittorf transference numbers of the alkali *chlorides* (at a concentration 1.2—1.3 molal), and the value for the Hittorf transference number of hydrochloric acid (at a concentration

[1] *Loc. cit.*

[2] For data on the mobility of the $\bar{I}_3$ ion see Burgess and Chapman, *J. Chem. Soc.*, 85, 1305 (1904); Bray and MacKay, THIS JOURNAL, 32, 914 (1910).

[3] See McBain (*Proc. Wash. Acad. Sci.*, 9, 1–78 (1907)), University of Toronto Studies, Papers from the Chem. Laboratories, No. 67, for a complete collection of the experimental data on transference numbers.

[4] Washburn, *Tech. Quart.*, 21, 164 (1908); THIS JOURNAL, 31, 322 (1909); Buchböck, *Z. physik. Chem.*, 55, 563 (1906).

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1.0 molal) which can be calculated from Buchböck's determination of true transference number and hydration. This comparison is made in Table V. The transference numbers for the chlorides and iodides at infinit dilution, calculated from conductivity data are also given in the table, and finally, values obtained for $N/10$ KI and $N/10$ NaI by Dennison,[1] using the method of Dennison and Steele and a value by Bein[2] for $N/20$ KI. This last is the only available datum for these iodides obtained by the Hittorf method without the use of membranes.

TABLE V.—TRANSFERENCE NUMBER OF THE ANION.

Halide of	Iodide, centrifugal.	Chloride, Washburn, Buchböck.	Iodide, Infinit dilution.[3]	Chloride, Infinit dilution.[3]	Iodide, Dennison.	Iodide, Bein.
K.....	0.514	0.518	0.507	0.503	0.514	0.505
Na.....	0.615	0.634	0.604	0.601	0.624	...
Li	0.732	0.722	0.665	0.662	...	...
H.....	0.184	0.160[4]	0.174	0.172	...	...

The agreement between the results presented in the table for the iodides with those for the chlorides is satisfactory. The greatest deviation occurs in the values for the two halogen acids. Hydrochloric acid,[5] however, is known to be abnormal in its behavior, since the transference number passes through a minimum at a concentration below normal, and the same effect might occur in hydriodic acid solution. Furthermore, since the electromotive force measured was so small in the case of hydriodic acid any constant error in the nature of a residual electromotive force might have had a large effect.

11. Summary.

In this article an apparatus and procedure have been described for determining transference numbers by the centrifugal method, first tried by Des Coudres. The method consists in the measurement of the electromotive force produced between electrodes placed at the central and peripheral ends of a rotating tube containing the electrolyte. An equa-

[1] Dennison, *Trans. Faraday Soc.*, 5, 165 (1909). It has been shown by Lewis, THIS JOURNAL, 32, 862 (1910), that the method of Dennison and Steele gives, after applying a calculable correction, the Hittorf transference number and not the true transference number as stated by Washburn.

[2] Bein, *Z. physik. Chem.*, 27, 1 (1898).

[3] These values for the transference number at infinit dilution were calculated from the latest conductivity data of Kohlrausch. *Z. Elektrochem.*, 13, 333 (1907).

[4] This value for the Hittorf transference number of molal HCl is calculated from Buchböck's determination of true transference number and hydration by the relation connecting those quantities as developed by Washburn. Washburn himself gives 0.18 for the Hittorf transference of HCl, a value which was taken from Kohlrausch's tables, but it is probably considerably too high. For HCl, 0.97 molal, Riesenfeld u. Reinhold, *Z. physik. Chem.*, 68, 440 (1909), obtain the value 0.155, and Hopfgartner, *Z. physik. Chem.*, 25, 115 (1898), obtains 0.159 for 0.9 molal HCl.

[5] Riesenfeld u. Reinhold, *Z. physik. Chem.*, 68, 440 (1909).

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tion can be derived, connecting this electromotive force and the transference number of the salt with the speed of rotation, the density of the solution, and the molecular weight and the "partial" specific volume of the substances involved, quantities which can be independently determined.

Some of the details of the construction of the rotating apparatus may have general interest. A distinctive feature of the apparatus was the method of driving the rotator (which had not been specially balanced) as a "spinning top," by hanging it below a fixed point of support. A simple arrangement of cords was devised for steadying the shaft of the rotating top and preventing precessional motion. A thrust bearing suitable for high speeds is also described. It consists of a series of ball bearings which distribute the total relative motion. An equation is given for calculating the dimensions of a rotating arm of uniform strength with the cross section increasing in size towards the center of rotation.

With this apparatus measurements were made of the electromotive force produced by the rotation of molal solutions of potassium, sodium, lithium, and hydrogen iodides. As predicted from the equations, the electromotive force was found to increase proportionately to the square of the speed of rotation. From the data the transference number was calculated for the four solutions, and found to agree as well as could be expected, with the available results of other methods of determination.

It was pointed out in connection with a kinetic derivation of the electromotive force relation, that the production of an electromotive force by centrifugal force is a proof of the presence of free ions in an electrolytic solution or at least of a certain degree of electrical polarization in the molecules.

The writer desires to express his gratitude to Professor A. A. Noyes, the Director of the Research Laboratory, whose interest and support made possible the completion of this research. Thanks are also due to Professor Elihu Thomson and Dr. Sanford A. Moss, of the General Electric Company, through whose kind offices was loaned the steam turbin used in this investigation. The writer also had the benefit of Dr. Moss's extensive experience with high-speed rotation, and is indebted to Professor George B. Haven, of the Institute, for his assistance in checking a large number of calculations of machine design which were made before the final apparatus was constructed.

The construction of the apparatus was made with the help of two grants of money from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences. The Chemical Department of the Institute was also very generous in its support of this costly research.

ANN ARBOR, MICH.

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MECHANICAL STIMULUS TO CRYSTALLIZATION IN SUPERCOOLED LIQUIDS.[1]

By S. W. Young.

Received October 21, 1910.

The phenomenon of the supercooling of liquids (which is here used to include the supersaturation of solutions) is apparently of virtually universal occurrence. It rarely, if ever, happens that a liquid cannot be cooled to some distance below its melting point without solidifying, and similarly almost any solution may be cooled to a temperature noticeably below its saturation temperature without the spontaneous appearance of crystals of the dissolved substance. In fact there is no positive evidence to show that these phenomena are not perfectly general. In the case of mixtures of two liquids, which at a definit temperature may separate into two layers, supercooling seems to be impossible. Investigations carried on in this laboratory with the assistance of Mr. Lovell Langstroth, with mixtures of several pairs of liquids, gave uniformly negative results.

Numerous attempts have been made to determin with accuracy the conditions under which crystallizations may occur in a supercooled system, and a rather voluminous literature has developed. A very complete abstract of it is to be found in various chapters of Ostwald's "Lehrbuch." The first positive result of these earlier investigations was to show that crystallization may be brought about without fail by the introduction into the supercooling system of a crystallin fragment, however small, of any solid phase in respect to which the liqu d is supercooled. If the liquid is supercooled in respect to more than one solid phase, any one of these may be produced at will by introducing a fragment of the particular phase desired. This is called crystallization by "seeding" or "inoculation." Somewhat later it was likewise definitly established that a fragment of a true isomorph was equally effective in bringing about crystallization, and that pseudomorphs were in no case effective.

Thus far the subject may be considered as a closed book. But quite the contrary is the case concerning our knowledge of the conditions which determin crystallization from supercooled liquids which are not seeded or inoculated. The investigation of this phenomenon of spontaneous crystallization, or crystallization without the introduction of crystallin fragments of the solid phase, has led to extremely conflicting and indeterminate results. Most of the recent investigations in this field have been conducted upon the assumption of the existence of what has been called the "metastable limit." The concept of the metastable limit was first introduced by Ostwald, and it has since been so generally accepted that it has rarely needed any defense.

[1] Read in abstract before the Division of Physical and Inorganic Chemistry at the San Francisco meeting of the Society, July 16, 1910.

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The significance of the idea of a metastable limit may be made clear in a few words. If a liquid be cooled ever so little below its melting point, it is to be looked upon as being in an unstable condition, capable of undergoing a change of aggregate state with the development of work or energy. The greater the amount of supercooling the greater the degree of instability. According to Ostwald, this unstable field may be divided into two parts. When the liquid is cooled below its melting point it remains through a certain range of temperature in what is called the metastable field or state. The distinguishing characteristic of this state is this: while a substance remains therein, it can never spontaneously crystallize, even under the influence of stirring and jarring. Only under the condition that a crystallin fragment of the solid phase be introduced can crystallization occur. As the liquid is more and more supercooled, however, it passes abruptly, at a definit temperature, out of this metastable state into what is called the labil or truly unstable state. In the labil field the conditions are entirely changed, and crystallization must spontaneously occur sooner or later. The time required may be very short or very long, and may in general be greatly reduced by a variety of causes, especially by agitation, and perhaps by the presence of dust particles. Precisely similar considerations apply to solutions.

Most of the investigators in this field, basing their work upon this distinction between metastable and labil, have attempted to determin, for a variety of substances and solutions, the value of the metastable limit, *i. e.*, that temperature at which a given substance passes from the metastable into the labil field. Until recently these attempts have met with but little apparent success. A single instance, that of the formation of the Liesegang rings,[1] appeared to give definit results. But even here the evidence is probably at fault, for more recent investigations seem to indicate that the formation of these rings is not at all, or at most only in part, a supersaturation phenomenon. In fact, Mr. G. D. Barnett, in this laboratory, has obtained Liesegang precipitates which were not rings at all, but spirals.

More recently the work of Miers, Hartley, Jones and others[2] in England and India has produced results that at first sight seem convincing. They sealed solutions of various salts, whose concentrations were known, into small tubes with added fragments of glass, platinum tetrahedra or other hard bodies. These tubes were then placed in a thermostat whose temperature could be very gradually lowered. As the cooling proceeded, the tubes were frequently shaken by hand, and the temperature at which crystallization occurred in each tube was noted. The results were reasonably constant for duplicates, and when plotted were found to lie fairly

[1] Morse and Pierce, *Z. physik. Chem.*, 45, 589.

[2] *J. Chem. Soc.*, 95, 1672, and preceding papers.

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well on curves overlying the normal solubility curves for the various salts, and running approximately parallel to these. These new curves are called the "supersolubility" curves for the various substances, and points upon them are considered by the authors to represent values for the metastable limit for solutions of the corresponding concentrations. When one considers that the metastable limit is defined as that temperature above which a given system cannot be brought to crystallization by mechanical shock or jar, and below which this is possible, the conclusion appears, on the face of it, to be justifiable.

de Coppet, in an extensive contribution,[1] summarizes his researches on the spontaneous crystallization of Glauber's salt and other substances. These researches have extended over thirty years, and as a result of his experience, de Coppet finds himself unable to accept the idea of the metastable limit. Without denying the virtual existence of metastable and labil distinctions, he considers the transition from the one field into the other to be a gradual one, and not the sudden one assumed by Ostwald. He interprets his results from the standpoint of the kinetic theory and the theory of probabilities, and concludes that the metastable state is to be looked upon as that state in which the probability of sufficient molecules under given kinetic conditions so arranging themselves that a crystallin aggregate may be formed, is indefinitly small in finit time. If the probability becomes very great the liquid is in a truly labil state, and between these two limits there may be a considerable range in which sporadic crystallization is likely to occur. For greater detail reference must be made to the original. In a closing paragraph de Coppet expresses his belief that mechanical agitation is unable to bring about crystallization except in the "fully labil" field, and that its principal effect is to "facilitate the development of germs already in the process of formation."

In this laboratory a very considerable amount of time has been devoted to the study of the phenomena of supercooling. Some of the results have been published, but much, and perhaps the greater portion of the work done has yielded nothing that seemed worthy of record, as the inconsistent and vagarious character of the results obtained produced more confusion than order. After having accepted for many years the hypothesis of the metastable limit, the writer was led, about three years ago, to the belief that it was probably fallacious and untenable, but on account of the apparent impossibility of obtaining consistent experimental data, was left for the time without any evidence wherewith to attack it, and it must be confessed, without very much hope of obtaining any. Finally, however, some observations upon the degree of supercooling,

[1] *Ann. chim. phys.*, [8] 10, 457.

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noted in a series of cryoscopic determinations, suggested a clue which, when followed up, led us to the present investigations.

Experimental Part.

The preliminary cryoscopic experiments involved in the work were very numerous, and for a time the results were very conflicting. They will be very briefly cited here. The experiments were all made with distilled water, without the addition of any solute. In the first place (all these experiments were carried out in an ordinary Beckmann apparatus) it was found that the amount of supercooling permitted was considerably less with a platinum stirrer than with a glass one. The majority of the results were fairly consistent, but showed frequent and occasionally large fluctuations. A stout copper wire used as a stirrer was found to admit of even less supercooling than the platinum one. In order to determin, if possible, what factors contributed to this result, a Beckmann apparatus was arranged with a mechanical stirrer, so that the character of the stirrer and the rate of stirring could be readily varied. With this apparatus a large number of observations were made, which, while still showing considerable fluctuations, yielded interesting results. In general, the values were nearly independent of the rate of stirring over a considerable range. In this series only copper and glass stirrers were used, and these were so arranged that there was friction between the stirrer and the stem of the thermometer. The following are a few of the typical results:

TABLE I.

Glass stirrer, θ[1].....	2.4	3.0	3.5	2.4	2.4	3.2	3.2	...
Copper stirrer, θ.....	0.9	0.9	0.9	0.8	0.8	1.0	0.9	1.0
Glass stirrer again, θ...	2.9	2.5	3.0	...	...	...	...	...

The simplest explanation of these results is that the friction between the stirrer and the thermometer is a potent factor in stimulating the crystallization of water, and that the copper-glass friction pair is much more effective than glass against glass. Similar results were obtained with stirrers of brass, platinum, iron and steel. The copper was always the most efficient.

Gas Stirrers.—In order to isolate so far as possible the influence of friction between two surfaces within the liquid, the apparatus was modified as follows: (1) A glass tube was introduced through the stopper, reaching nearly to the bottom of the Beckmann tube, through which a continuous stream of gas could be maintained. This produced regular and efficient stirring, and permitted the independent observation of the effect of the friction parts; (2) a straight rod was substituted for the usual Beckmann stirrer, and so arranged that it could play through a

[1] θ is used throughout to represent the amount of supercooling in centigrade degrees.

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ring which was suspended in the liquid, by means of a rigid attachment to the stopper. Rods and rings could be easily made of any desired materials, and a considerable variety of experiments were thus made possible. A sketch of the apparatus is shown in Fig. 1.

A is the rod whose lower end plays through the ring *B*. *C* is the tube for introduction of the gas. *D* is a thermometer reading to tenth degrees.

The conduct of this apparatus was first observed while using the gas stirrer alone, *i. e.*, without the introduction of the rod and ring. Hydrogen, oxygen and air were successively tried as stirrers, and rather remarkable results were obtained. The values obtained for the supercooling of water, when agitated by continuous streams of either oxygen or hydrogen, were extremely uniform, with no appreciable differences for the two gases. A large number of determinations were made, and with remarkably few exceptions all of them lay between 5.4 and 5.6 for the value of θ. Within wide limits the results were independent of the rate of flow of the gas, as well as of the form of the aperture through which the gas was admitted. With air, even when fairly well cleaned, the results were rather erratic. Hydrogen, being the easiest gas to generate, was used in the following experiments. As a safeguard it was washed by passing in through a column of wet absorbent cotton about three feet long.

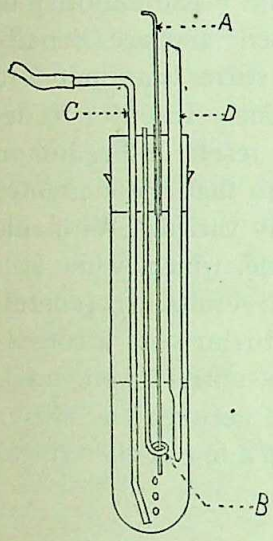


Fig. 1.

Influence of the Character of the Water.—In general, as has been stated, all experiments were made upon distilled water. At this point, however, it seemed worth while to get some little idea of the way in which different specimens of water would conduct themselves toward the hydrogen stirrer. The investigation has not gone far, but has given some interesting results. A pure, clean drinking water gives values in close agreement with those for ordinary distilled water, namely, close to 5.5°. On the other hand, a sample of dirty irrigation water carrying considerable silt gave values lying closely around 4.6°, *i. e.*, nearly a whole degree less of supercooling was possible. After being carefully filtered, however, this water gave regularly values coinciding with those for distilled water. The addition of small amounts of powdered emery or pumice to distilled water reduces its θ value greatly, and this effect may be removed by filtration. Following is a series of observations upon this point. In all cases the stirring was by hydrogen alone.

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TABLE II.

	θ	θ	θ		θ
Distilled water, no addition.	5.4	...	...	Distilled water, emery filtered out	5.4
Distilled water, emery added	1.8	1.9	1.9	Distilled water, pumice added.....	2.1
				Distilled water, pumice filtered out	5 5

Purification of the water by boiling, or even by redistillation, produces no noticeable effect. If, however, the water is purified by direct distillation into a tube freshly cleaned with chromic acid mixture, and especially if the tube is thoroughly steamed out before allowing the water to condense; under these conditions a very considerable increase in the supercooling is found. It is best to exclude air also, which may be done by keeping a continuous stream of hydrogen flowing through the apparatus, even during the distillation. By this means what may be called "hydrogen values" for θ have been obtained as large as 8.5°. Carefully prepared water hammers may be cooled to temperatures as low as —15° if precautions are taken to avoid mechanical shocks. The whole matter of the effect of mechanical and other impurities will be made the subject of special investigation.

Rod and Ring Friction Experiments.—A very large number of determinations were next made with the rod and ring apparatus above described. A few only of these results are shown in Table III:

TABLE III.

Nature of stimulus.	θ	θ	θ	θ	θ
Hydrogen stirrer alone.....	5.4	...	...	...	...
Copper ring-copper rod.....	1.6	1.2	1.25	1.2	1.2
Copper ring-platinum rod.....	2.8	2.5	2.9	...	...
Copper ring-iron rod.....	2.7	2.85	2.6	...	...

Upon removing the metal parts, the hydrogen value returned to 5.5. The results for platinum and iron against copper are virtually the same, while those for copper against copper are much smaller. At first thought this might seem explainable by the fact that in general the friction coefficients between like bodies is greater than that between unlike ones. Certain incidental observations, however, led to the belief that factors as yet uncontrolled were concerned. Owing to the fact that there was always considerable space between the rod and the ring, considerable impacts between the two were always possible. It was thus considered wise to so modify the apparatus that it became still more purely frictional in its action. The first modification tried was the substitution of a piece of tubing for the ring. The tube was of such size that the rod would just easily pass through it, and in order that there should be no clattering between it and the rod, it was placed slightly out of alignment with the latter. Three sets of these friction parts were made, one of tool steel, one of brass and one of glass. Following (Table IV) are some of the results obtained:

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TABLE IV.

Friction parts tool steel.	Tool steel + emery.	Brass.	Glass.	Glass (rough).[1]
θ = 1.7	1.1	2.5	4.0	1.3
" 2.2	1.25	2.3	4.4	2.0
" 2.2	1.2	4.4	5.0	1.5
" 2.05	1.1	2.9	4.7	1.4
" 2.70	1.3	2.85	...	2.0
" 2.30	1.45	3.1	...	...
" 1.60	1.30	3.4	...	...
" 2.30	1.35	3.1	...	...
" 2.35	1.20	4.4	...	...
" 3.00	1.35	2.9	...	...

In the experiments with this apparatus the freezing always started at the point of friction, which was shown by the fact that the first evidence of freezing was the adherence of the rod to the collar. The results still show very considerable fluctuations, in fact greater ones as a rule than were shown in the rod and ring apparatus. Otherwise their main significance lies in the fact that they clearly show the greater effect of friction between rough than between smooth surfaces of a given substance (see results with glass).

Rotary Friction.—Still another type of apparatus was tried, in the hope of finding a frictional device that would yield more definit and consistent results. This was a rotary frictional contrivance, the essential features of which are shown in Fig. 2. The rod *A* of any desired material is turned to a conical tip at either end. The lower end is seated in a similarly formed conical bearing, *B*, which is likewise of any desired material. The copper end is also seated in a cone bearing carried in the under side of a lever, *C*, whose fulcrum is at o. By means of the movable weight at *E*, the load upon the bearing *B* may be altered at will. The rod is rotated at any desired speed by a belt connecting the pulley *F* with a motor shaft.

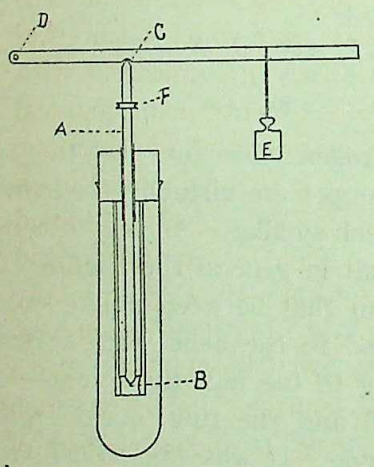


Fig. 2.

The results obtained with this apparatus were very unexpected, and for a time seemed wholly inexplicable. Without giving the voluminous data obtained, the conclusions may be summarized as follows:

(1) Both tool steel and brass friction parts give results that are nearly independent of the rate of rotation, although a slight increase in efficiency with increasing velocity is noticeable in all cases.

[1] Roughened with emery paper.

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(2) With tool steel the result of increasing the load on the counterpoise was to decrease the values for the supercooling. This is of course what is naturally to be expected, if it is assumed that friction is the effective impulse.

(3) Brass parts, however, gave results of the opposit character; that is, as the weight upon the counterpoise was increased the value for the supercooling also increased, and this in a quite noticeable degree. A repetition of the measurements with tool-steel parts showed that the same phenomenon may occur as with brass, but in this case the apparatus must be in continuous use for a long time before the values under large load fall below those under light load. These results, conflicting as they seem, led to a train of thought which finally cleared up the whole problem.

If one considers what must be the nature of friction occurring between two solid surfaces, it seems probable that it will always consist of a series of small jumps and impacts, similar to the effect produced when one rubs the finger over a pane of glass, or around the rim of a goblet, in such a way that the glass is set in vibration. Only in mathematically smooth surfaces, probably, can such a thing as "pure friction" be imagined. The amplitude of the jumps and the magnitude of the resulting impacts will depend upon a variety of factors, among the more important of which will be the hardness of the bodies and the physical character of the surfaces. It has been noted above that friction between rough surfaces is more efficient in stimulating crystallization than that which occurs between smooth surfaces of the same material. This, in connection with the above considerations, leads to the inquiry as to whether mechanical impacts may not be the true stimulus to crystallization in all of the above experiments, and friction only efficient in so far as it is to be looked upon as a series of impacts. Such a theory readily explains the results obtained with the rotary apparatus. The brass friction parts, being soft, grind themselves a smooth seating in a comparatively short time, especially under a heavy load. The magnitude of the impacts is thus rapidly reduced, and the conduct of the apparatus is perfectly explained. With tool-steel parts the grinding of a smooth seating will be a matter of much greater time, even under a considerable load. The immediate effect of increasing the load on the counterpoise will be an increase in effective stimulus, and this may persist for a long time. Finally, however, as the seating becomes smoother the effective stimulus will fall off, and in time may become less than had been previously observed under a lighter load. This is also in accordance with the observations made.

Impact Experiments.—If these considerations are correct and crystallization is stimulated rather by impact than friction (in the ordinary sense), experimental demonstration of the fact should be comparatively

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easy. With this in mind an apparatus was constructed which worked on the principle of a stamp mill. Fig. 3 shows the essential features of this apparatus. The stamp consisted of the steel rod *A*, at the lower end of which was attached a collar into which the bit *B* could be cemented. This bit is interchangeable, so as to allow of the investigation of any desired substance. To the upper end of the rod was cemented the glass tube *C*, which could be loaded with any desired quantity of mercury, thus producing considerable variation in the weight of the stamp. The stamp could be raised to any desired height and allowed to drop through the guide *D*, thus producing impact between the bit and the anvil *E*. Upon the anvil was cemented a flat disc, *F*, which served as the striking surface for the bit. This disk was also interchangeable, and could be of any desired material. In operating the apparatus, an arrangement was devised whereby the stamp could be kept in continuous action at any height by means of a motor. Thus a continuous series of impacts of nearly constant value was produced within the liquid under investigation. The liquid was continually agitated by means of the hydrogen stirrer, and being surrounded by a cooling bath so arranged that the temperature fell from one-quarter to one-half degree per minute, that temperature was noted at which crystallization occurred. This was the value for the supercooling possible under the influence of the given mechanical stimulus.

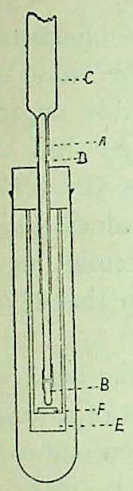


Fig. 3.

Preliminary investigations were made with a considerable variety of impact materials. With most substances the continued impacts produce such marked changes in the character of the impact surfaces that the results were somewhat inconsistent. This is true of all soft metals such as brass, and even soft steel. It is especially true of very hard substances which are also brittle. A series of measurements were made with corundum impact parts, and gave the most uncertain results of all. As a result of these preliminary experiments, tool-steel parts, mercury-hardened, were found to give thoroughly reliable results, especially after thorough smoothing and polishing with crocus. After considerable use it was found advisable to repolish. In the following series of measurements such an impact pair was used. The disk was flat, and the bit was turned into a hemispherical tip so that slight inaccuracies in the guiding of the stamp would not affect the area of the surface of impact. This apparatus, while rather crude and shaky, gave unexpectedly reliable results, which are tabulated below. Measurements were made upon water, benzene, and a concentrated solution of the hexahydrate of calcium chloride.

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TABLE V.

	Distilled water.			Benzene.		
Drop.....	1 cm.	1 cm.	5 cm.	3 mm.	1 cm.	5 cm.
Weight.....	40 g.	100 g.	100 g.	40 g.	140 g.	100 g.
$W \times D$.....	40	100	500	12	40	500
Values of θ....	2.9	0.8	0.1			
	2.9	0.8	0.1	0.4	0.3	0.2
	2.7	0.9	0.1	0.4	0.3	0.2
	2.9	0.8	0.1	0.4	0.3	0.2
	3.0	0.7	0.1			

Owing to the slowness of the rate of crystallization in the immediate neighborhood of the melting point, it is probable that the values for θ recorded in the last column for water are considerably too large.

The hydrogen value for benzene was found to be about 3°. Both the rate of crystallization and the latent heat of fusion for benzene being less than for water, an even greater lag is to be expected. In tubes which were supercooled but one-tenth of a degree, crystallization could be forced by "throwing" the stamp. This was accomplished by lifting the stamp by hand and forcing it down upon the anvil, just as one would throw the ramrod in loading a muzzle-loading gun. In this case, of course, no definit idea of the value of the impact can be had.

TABLE VI.—MEASUREMENTS ON FUSED $CaCl_2.6H_2O$.

Drop.....	1 cm.	1 cm.	5 cm.	Forced by throwing.
Weight.....	40 g.	100 g.	100 g.	
$W \times D$.....	40	100	500	...
Values of θ.....	8.4	2.7	2.2	1.6
	7.4	2.6	2.0	1.5
	11.0	2.6	2.0	1.5
	7.0	2.9	...	...

The calcium chloride used was a commercial preparation showing a melting point of 28.9°, and consequently carried some little excess of water. It showed a hydrogen value of about 21°. The discrepancies in the values found in column 1 are probably due to two causes: (1) the apparatus itself had become very badly used up, especially as a result of so much "throwing;" (2) at the temperatures corresponding to these values, the calcium chloride is already very sensitive to external jars. In fact, by running the apparatus without the stamp, *i. e.*, allowing the lifting and dropping device to run alone, the jarring would usually start the crystallization when the supercooling was about 10°. Of course only such results are reliable as are obtained when the shock of the stamp transcends all others. Consequently the values in column 1 are doubtful.

Discussion of the Results.

In attempting to plot the results of the above measurements, the question immediately arises as to what function of the weight and drop dis-

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tance is to be used. Until more data can be gathered, but little ground for choice is apparent. Whether the stimulus is directly mechanical or perhaps due to local high temperature or pressure is uncertain. Assuming, however, that it is a purely mechanical effect, it is still impossible to say whether the energy developed, *i. e.*, the "impact" value which is equal to the mass × the height, or the impulse value, *i. e.*, the mass × the square root of the height, is to be considered as a measure of the stimulus. It is perfectly possible even that neither of these functions is the true one. The fact that the apparatus used was so crude, and also that it had become at this point so shaky in its action, made it impossible to carry out the necessary precise measurements for the determination of this point. A new and much improved apparatus is in process of construction, and it is hoped that with its aid conclusive data may be obtained. In the meantime the results already obtained have been plotted in terms of the impact values, rather than the impulse values. For the general interpretation of the results the matter is not of great importance, since the general form of the impulse and impact curves is not essentially different.

In Fig. 4 are plotted the relationships between the θ values and the impact values for water, benzene and the hexahydrate of calcium chloride.

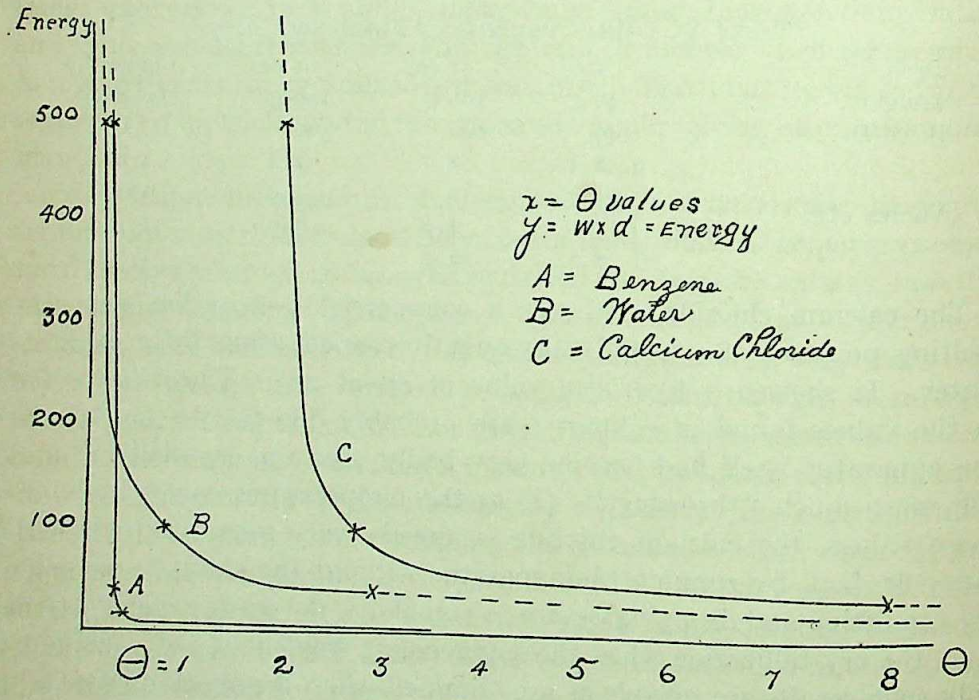


Fig. 4.

These curves are manifestly asymptotic to both axes, and possess, at least superficially, the characteristics of hyperbolas of very short focal distance. The curve for water is extrapolated along the X-axis in such

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a way that the impact value would be almost zero at a θ value of 16. This seems fairly justifiable in consideration of the fact that when supercooled to this extent, water becomes extremely sensitive to such slight jars as may occur ordinarily about a laboratory.

As a result of these experiments it seems to be no longer necessary or even justifiable to assume the existence of a metastable limit in the generally accepted sense, nor does it seem desirable to distinguish between a metastable and a labil field in the de Coppet sense. The whole unstable field is labil and crystallization may be brought about in any portion of it by the production of sufficient mechanical shock. In many cases the shock required may be enormous even in very considerably supercooled systems. This is undoubtedly the case with Glauber's salt. A few experiments were made with a solution of this salt, which was saturated at 25°. Glauber's salt could be forced to crystallize from such a solution at temperatures below 7°, but only with the severest shock that could be given by throwing the stamp. Thus such a solution may supercool 18° under the influence of such shocks as would allow no measurable supercooling with water.

On the other hand, an inspection of these curves shows very clearly why the idea of the metastable limit has for so long seemed plausible, and why the values for the supercooling limit frequently group themselves very closely together. The Y-arm of the curves is for a long time nearly vertical, and throughout a more or less considerable range of temperature the shock required to force crystallization is very large. Along the X-arm the reverse condition holds, and a large variation in temperature corresponds to a very small variation in impact value. These two nearly straight lines are connected by the sharp curves found in the neighborhood of the foci. Thus the transition of the system from a condition of very slight sensitiveness to shock to one of very great sensitiveness, while continuous, is nevertheless very rapid, and it is undoubtedly this short, sharp curve which has heretofore been mistaken for the metastable limit. If this sharp turn, which may perhaps as well be called the "transition" curve (although it probably has not the attributes of a true transition curve), lies at impact values corresponding to ordinary laboratory disturbances, and perhaps to the activity of dust particles, fairly agreeing values would be obtained from experiments made at rest. This is shown more or less in the conduct of benzene. If the transition curve lies at higher impulse values, such as correspond to shaking and stirring, a comparatively closely grouped set of results will be obtained by working under those conditions, which is shown in the conduct of the hexahydrate of calcium chloride. If it lies at very high values, conduct like that of glycerol and alcohol, which rarely crystallize, even when highly supercooled, is to be expected.

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The results of the shaking experiments of the English chemists, which were referred to in the early part of this paper, are thus to be looked upon as approximately constant results obtained with approximately constant maximum shock. They find some substances unsuited to the determination of the metastable limit by their method, which presumably means that their method did not give sufficient impulses to enable them to reach the neighborhood of the transition curves for those substances. It is interesting to note that their values for the metastable limit for water (from solutions) lie closely about six-tenths of one degree. This temperature lies upon the transition curve for water as determined from these experiments.

If one desires any mechanical analogy to explain the phenomena under consideration, the following seems to serve the purpose fairly well. One may consider the crystallizing forces in a liquid to be roughly analogous to the magnetic forces in a field. At temperatures above the melting (or saturation) point, these directive forces are overcome by the disruptive forces, mainly probably, the kinetic energy of the molecules. At the melting point, the molecules are in such a condition that the directive and disruptive forces just balance one another. At temperatures below the melting point the directive forces are the greater, but the molecules being also under the influence of resistive forces such as viscosity, are like the iron filings in a weak field, unable to arrange themselves into the stable form until assisted by a mechanical jar.

Interesting complications occur when the supercooled liquid is in a position to yield more than one solid phase. Ostwald has suggested, as covering such cases, the rule which bears his name, and which states that when two or more solid phases may separate from a liquid, it is always the least stable one that appears first. While often giving correct conclusions, the rule is subject to frequent violation. From the above results it would seem reasonable to assume that each of the two or more possible phases would have its own impact curve, and that any phase might be produced at will, according to the impact given. This has been accomplished in the case of Glauber's salt and the heptahydrate of sodium sulfate.

A solution of Glauber's salt was prepared, which was saturated at 25°. Such a solution would also be saturated with heptahydrate at 7.5°. Below 7.5° the solution is thus in a position to yield two solid phases. With the hydrogen stirrer it yields heptahydrate invariably at about 2°. By means of increasing shocks with the stamp apparatus, heptahydrate may be brought down at temperatures as high as 6°. In this connection it is to be noted that Hartley's value for the metastable limit of the heptahydrate in such a solution is —4°.[1] At temperatures

[1] *J. Chem. Soc.*, 94, 825.

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below 7° Glauber's salt may be brought down in preference if the shocks are sufficiently great, but this is a matter of much difficulty and required the severest possible throwing of the stamp. Thus at temperatures below 6 or 7° moderate shocks will force the crystallization of heptahydrate, while more severe ones will bring down Glauber's salt. Since the solution is saturated as to heptahydrate only at temperatures below 7.5°, it follows that the impact curve for this particular solution with respect to heptahydrate must become asymptotic to the Y-axis at this temperature. Similarly the impact curve for Glauber's salt in the same solution becomes asymptotic to the Y-axis at 25°. These facts, in connection with the lower impact values for heptahydrate below 6 or 7°, show that the two impact curves in question must cross one another at a temperature in the neighborhood of 6 or 7°. At temperatures below this point Glauber's salt will require the greater impact, while at temperatures above this same point, the heptahydrate will require the greater impact. If these considerations are correct, it would seem that the separation of any one of all the possible solid phases from a supercooled liquid is a matter which is determined by the course of its impact curve with respect to those of all other possible phases. In general, by cooling a liquid at rest, that phase will first appear whose impact value first reaches a very small magnitude. The curves in Fig. 5 show this relationship. It is to be added that these curves are of only a qualitative character. Further, it is not necessary that such pairs of impact curves should intersect.

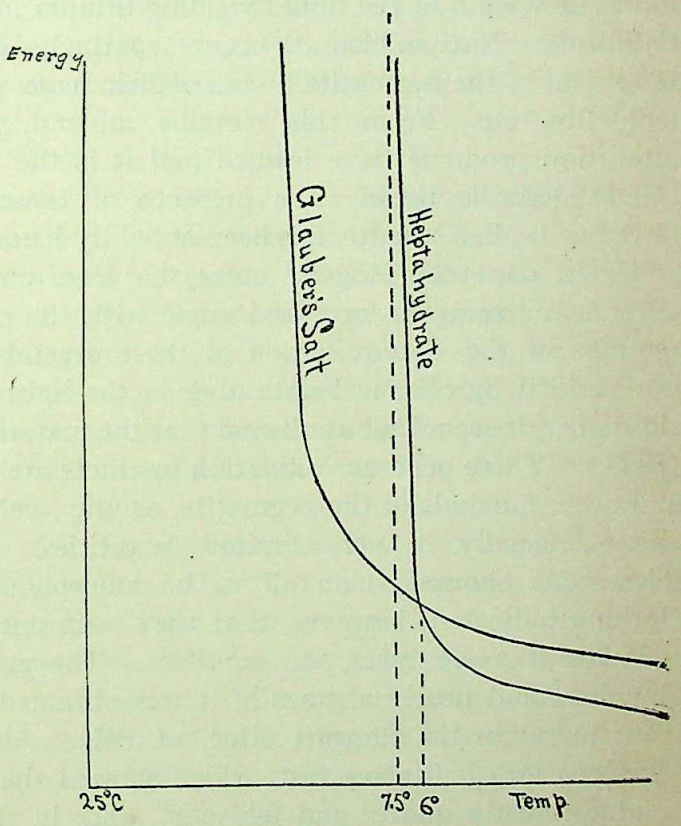


Fig. 5.

The above considerations apply only when other influences which may cause crystallization are excluded, or at least are present only in such degree that the efficiency of the mechanical impact used is greater. That other influences do exist will not be denied by any one who has worked

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in this field. Oftentimes with some substances, what seem to be wholly fortuitous cases of crystallization, will occur in liquids at rest, under such conditions that a very large mechanical shock would be required to accomplish the same result. As to the nature of these influences but little can be said at the present time. Investigations are under way which it is hoped may throw some light on the subject. Also the researches upon the mechanical stimulus are being extended.

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BISMUTH OCHERS FROM SAN DIEGO CO., CALIFORNIA.

BY WALDEMAR T. SCHALLER.

Received November 28, 1910.

Introduction.—The bismuth ochers which are herein described were found at several of the mines yielding lithium minerals in San Diego Co., California. Native bismuth occurs sparingly, as a primary component, in several of the pegmatite bodies which have produced gem tourmalin, lepidolite, etc. From this metallic mineral, a number of secondary alteration products have formed and it is the purpose of this paper to briefly describe these. The presence of these bismuth ochers, which have been called bismite, has been noted by Kunz[1] and also by the writer.[2] A recent paper by Rogers[3] notes the occurrence of bismite in distinct crystals, agreeing in form and angle with the artificial Bi_2O_3. The correctness of the determination of these crystals as bismite (Bi_2O_3) was not verified by chemical data and, in the light of the facts set forth in this paper, it seems not at all sure that the material is the oxide of bismuth (Bi_2O_3). These ocherous oxidation products are found coating the quartz and other minerals of the pegmatite, as gray, yellow, or green pulverulent masses, usually in very limited quantities. Examination under the microscope showed them all to be amorphous, and not transparent. Nothing indicated, however, that they were not homogeneous.

Yellow Bismuth Ocher, Stewart Mine.—The yellow powder is the most abundant and nearly a gram of it was obtained for analysis from specimens found in the Stewart Mine, at Pala. About a quarter of it was sacrificed for qualitative tests which showed the presence of an insoluble residue (mostly quartz and feldspar), and, in the solution, of abundant bismuth and vanadium with very small quantities of silica, alumina and lime. A small amount of water was given off when the ocher was heated in a closed tube. No carbon dioxide was given off on dissolving the

[1] G. F. Kunz, "Native Bismuth and Bismite, from Pala, California," *Am. J. Sci.*, [4] 16, 398 (1903).

[2] W. T. Schaller, "The Tourmaline Localities of Southern California," *Science*, 19, 266 (1904).

[3] A. F. Rogers, "Minerals from the Pegmatite Veins of Rincon, California," *School of Mines Quart.*, 31, 208 (1910).

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mineral in hydrochloric acid, and bases other than those mentioned could not be detected in the solution.

The quantitative analysis of the yellow bismuth ocher from the Stewart Mine gave the following values; the ratios obtained therefrom are also given.

ANALYSIS AND RATIOS OF YELLOW BISMUTH OCHER, STEWART MINE, PALA, CALIFORNIA.

	Bi_2O_3	64.43	0.139 or 2 × 0.0695
	V_2O_5	12.11	0.067 or 1 × 0.067
Gang	sol. in HNO_3	2.27	
Gang	insol. in HNO_3	17.63	
H_2O	at 107°	0.32	
H_2O	at 210°	0.24	0.204 or 3 × 0.068
H_2O	on ign.	3.43	
		100.43	

The ratios yield sharply the formula $3H_2O.2Bi_2O_3.V_2O_5$ which may be interpreted as $BiVO_4.Bi(OH)_3$, forming a basic hydrous bismuth vanadate. This is also structurally interpretable, Professor F. W. Clarke suggesting the following:

$$HO.Bi:VO_4.Bi:(OH)_2$$

Based on the evidence so far shown, one would be almost justified in describing the yellow ocher from the Stewart Mine as a distinct new mineral species with the formula just given. In fact, many new (supposed) species have been proposed on evidence weaker than that here given. On extending the investigation of these ochers, however, results were obtained that show conclusively that the above analyzed bismuth ocher is not uniform in composition, does not possess the formula deduced and is, in all probability, a mixture of bismuth vanadate and bismuth hydroxide.

Yellow Bismuth Ocher, Pala Chief Mine.—A sample of coherent yellow ocher was found at the Pala Chief Mine, which resembled that from the Stewart Mine in almost every way. An analysis of this was made in order to verify the composition deduced from the analysis just given. Very unexpectedly the composition of the second sample of ocher was found to be different from the first and to agree in composition with pucherite, $BiVO_4$. A fifth of a gram gave, on analysis, the results shown below.

ANALYSIS AND RATIOS OF YELLOW BISMUTH OCHER, PALA CHIEF MINE, PALA, CALIFORNIA.

	Bi_2O_3	66.14	0.143
	V_2O_5	25.80	0.142
	Insol. gang	7.37	.....
H_2O	at 107°	0.21	.....
H_2O	at 240°	0.32	.....
H_2O	on ign.	0.84	.....
		100.68	

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The ratios yield sharply the formula $Bi_2O_3.V_2O_5$, which is the mineral pucherite. This appears to be the first noted occurrence of pucherite in the United States and the first time that amorphous pucherite has been found. The small amount of water retained above 107° may have come from the insoluble gang. Massive pucherite probably also occurs at the Tourmaline Queen Mine, Pala, but its quantity is entirely insufficient for any quantitative work.

Gray Bismuth Ocher, Stewart Mine.—One specimen of quartz collected from the Stewart Mine, Pala, showed a small coating of a grayish material containing a few yellow spots scattered through it. A quantity of the material was scraped off with a knife but only 0.0953 gram substance could be obtained. An analysis made on this small amount gave the following values:

ANALYSIS OF GRAY BISMUTH OCHER, STEWART MINE, PALA, CALIFORNIA.

	Bi_2O_3	64.9
	V_2O_5	0.8
Gang	sol. in HNO_3	9.5
Gang	insol. in HNO_3	13.5
H_2O	at 107°	0.4
H_2O	at 240°	0.3
H_2O	on ign.	11.4
		100.8

As the analysis shows, only a small amount of vanadium is present and this is doubtless due to the presence of a little pucherite as shown by the small yellow spots in the original sample. Beside the gang, only bismuth oxide and water are present and this gray bismuth ocher is doubtless a bismuth hydroxide. Before considering the ratios, however, a little water should be deducted for the gang soluble in nitric acid, which is probably a clay comparable to the halloysite occurring here so abundantly. This halloysite, as shown by my analysis,[1] contains nearly 19 per cent. of water, of which one-third is given off at 107°. However, assuming that the 9.5 per cent. of soluble gang was ignited halloysite, there would be about 2.2 per cent. of the total water belonging to this gang. As some water was also given off by the insoluble gang, it may be safely assumed that nearly 3 per cent. of the total water found belonged to the gang and not to the bismuth ocher. Readjusting the analysis on this basis we have the following values.

The ratios agree fairly well with the formula $Bi_2O_3.3H_2O$, considering the quality and quantity of material and the uncertain nature of the assumptions made with regard to the water of the gang. The gray bismuth ocher may then be classed as a bismuth hydroxide, $Bi(OH)_3$,

[1] W. T. Schaller, "Notes on Some California Minerals (Halloysite)," *Am. J. Sci.*, [4] 17, 191 (1904).

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and the yellow ocher from the Stewart Mine is simply a mixture of $Bi(OH)_3$ and $BiVO_4$, the apparent rationality of the molecular ratios being only accidental.

READJUSTED ANALYSIS AND RATIOS OF GRAY BISMUTH OCHER, STEWART MINE, PALA, CALIFORNIA.

Bi_2O_3	64.9	0.140 — 0.004 = 0.136 = 1.0
V_2O_5	0.8	0.004 — 0.004 =
H_2O (ocher)	9.1	0.506 = 0.506 = 3.7
H_2O (gang)	3.0	
Gang	23.0	
	100.8	

Conclusion.—The appearance of most of the samples of bismuth ocher that I have from this general locality is such as to suggest that most of them are mixtures of the hydroxide and vanadate of bismuth. They certainly are not bismite (Bi_2O_3). The presence of considerable vanadium in these yellow ochers was also established qualitatively for specimens from the Tourmaline Queen Mine at Pala, and from the Victor Mine at Rincon. Moreover, all the yellow specimens from the Stewart Mine, at Pala, that were tested showed the presence of vanadium. The source of the vanadium is probably to be found in the surrounding altered gabbro.

Method of Analysis.—The method of analysis was as follows: The mineral was heated in a porcelain crucible at different temperatures (as given) to constant weight and finally ignited by a low flame. The water was thus determined by loss, but its presence and the absence of carbonic acid was determined qualitatively for each sample analyzed. The ignited mass was dissolved in nitric acid, the insoluble residue filtered off and the bismuth precipitated by hydrogen sulfide. The bismuth was finally precipitated as carbonate and weighed as Bi_2O_3. The combined filtrates containing the vanadium were evaporated to dryness and the vanadium and soluble gang weighed as a check on the subsequent determinations. The vanadium was then separated by a current of dry hydrochloric acid gas, the vanadium oxychloride formed was collected in water and, after evaporating down with sulfuric acid, was reduced and titrated with permanganate. The residue from which the vanadium was driven off by hydrochloric acid gas, was ignited and weighed as the residue soluble in nitric acid. It consisted chiefly of silica and alumina with some lime.

Composition of Bismite.—A review of the literature on bismite or bismuth ochers free from carbonate shows only two analyses on which the existence of the natural anhydrous oxide of bismuth is based. The first is by Suckow[1] (1848) who gives the composition of bismuth ocher, free from water and carbonic acid, as follows: Bi_2O_3, 96.5; As_2O_3, 1.5;

[1] See C. Hintze, *Handbuch d. Mineralogie*, 1, 1246 (1904), for references.

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brown iron ore, 2.0; total, 100. The analysis is certainly far from satisfactory. The second analysis is by Carnot[1] who gives 96.70 per cent. Bi_2O_3 with the remainder distributed over eight compounds, including 0.95 per cent. H_2O, also SO_3, HCl, CO_2, etc. While indicating the probable presence of Bi_2O_3, the existence of the simple oxide can hardly be considered as established by the analysis of Carnot. As the first natural crystals of bismite described do not agree[2] with those artificially prepared, it seems doubtful whether Bi_2O_3 actually occurs in nature. The apparent identity of the natural crystals described by Rogers[3] with the artificial crystals of Bi_2O_3 is rendered somewhat questionable by the lack of chemical data on his crystals and by the evidence of the composition of the San Diego County ochers, as shown in this paper.

Summary.—The chief points brought out in this paper may be briefly summarized as follows:

(1) The existence of natural Bi_2O_3 has not been established.

(2) Natural bismite or bismuth ocher, when pure, is more probably a bismuth hydroxide.

(3) The bismuth ochers from San Diego County, California, are either a bismuth hydroxide or bismuth vanadate, pucherite, or mixtures of these two.

(4) Pucherite has been found noncrystallin and determined for the first time in the United States.

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RECENT WORK IN INORGANIC CHEMISTRY.

BY JAS. LEWIS HOWE.

Received December 10, 1910.

The problem of chemical formulas and nomenclature of inorganic compounds, with especial reference to indexing, is discussed by M. K. Hoffmann,[4] and the system used in his recently published *Lexicon der anorganischen Verbindungen* is described. Without attempting changes which can be considered radical, a logical and unambiguous system is worked out, which deserves general consideration.

The solubility of gases in metals has been studied by Sieverts.[5] Nitrogen dissolves in no metals, but reacts with several, forming nitrides. Carbon monoxide dissolves in both solid and fused nickel and also in cobalt, but not in copper. Sulfur dioxide is soluble in fused copper but insoluble in solid copper. Oxygen is soluble in silver but not in gold. Hydrogen is the most generally soluble of gases, but is not soluble in silver, gold, tin, and many other metals. Its solubility in copper is in-

[1] See Hintze's Handb., *loc. cit.*, for references.

[2] W. T. Schaller and F. L. Ransome, "Bismite," *Am. J. Sci.*, [4] 29, 173 (1910).

[3] *Loc. cit.*

[4] *Chem.-Ztg.*, 34, 73.

[5] *Z. physik. Chem.*, 68, 115; 74, 277. *Ber.*, 43, 893. *Z. Elektrochem.*, 16, 707.

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creased by the addition of nickel and platinum in which it is soluble, and decreased by tin and aluminium in which it is insoluble. In the occlusion of gases by metals adsorption plays very little part, as the phenomenon is independent of surface area, and its true solubility. This solubility varies with the square root of the pressure. Greenwood[1] has determined the boiling points of several metals, using a resistance furnace and graphite, or magnesia-lined crucibles. The following figures were obtained:

Magnesium	1120°	Lead	1525°	Chromium	2200°
Bismuth	1420°	Aluminium	1800°	Tin	2270°
Antimony	1440°	Manganese	1900°	Copper	2310°
		Silver	1955°	Iron	2450°

Some two years ago Hasslinger announced a new form of "tin pest" which has been since investigated by Cohen, who finds that it has nothing in common with the ordinary "disease" of tin, but is due to mechanical stress, and to it he gives the name of stress-sickness (Forcierkrankheit). He now finds[2] that this condition is not peculiar to tin, but that all metals assume a metastable condition by being worked, and that this condition can be transmitted by contact infection. In his experiment with tin, he etches a smoothed surface of rolled tin by a moment's action of $KClO_3$-HCl mixture and presses on the carefully cleaned surface a clean piece of tinfoil. On heating to 184°, the etched surface of the tin is reproduced on the foil. The phenomenon was repeated with lead, zinc brass and bismuth.

The experiments of Naumann on reactions in non-aqueous solutions have been continued[3] by the investigation of the action of ammonia and hydrogen sulfide on the metals of the second (analytical) group in ethyl acetate solution. The most marked departure from aqueous solutions is that hydrogen sulfide generally precipitates the sulfide only in the presence of ammonia, though stannous sulfide is precipitated from stannous chloride solution by hydrogen sulfide alone. Ammonia generally precipitates ammines, which are insoluble in ethyl acetate.

Group I.—By heating various elements and compounds with dry sodium formate in intimate mixture, Vournasos[4] finds the nascent hydrogen is given off much more reactive than ordinary hydrogen. Red phosphorus gives phosphine, sulfur gives hydrogen sulfide, free or combined arsenic, arsine; sodium antimonite gives but little stibine, and silicon does not react, though both the sulfide and chloride of silicon give hydrogen silicide. Nitrides give ammonia, cyanides, hydrocyanic acid, and carbides of the alkalies give acetylene. With boron nitride and also with a mixture of boron oxide, sodium formate and metallic sodium, a small amount of hydrogen boride was obtained, which was, however, not isolated.

In 1863, Rose described a suboxide of copper, Cu_4O, which has since retained its place in text books. Moser[5] has repeated the work of Rose in the light of modern methods and finds no evidence of the existence of this oxide, Rose's compound being a variable mixture of cuprous

[1] *Proc. Roy. Soc. London*, (*A*) 82, 396.
[2] *Chem. Weekblad*, 6, 625, 881.
[3] *Ber.*, 43, 313.
[4] *Compt. rend.*, 150, 464, 922.
[5] *Z. anorg. Chem.*, 64, 200.

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oxide and copper. On the other hand the work of Etard and of Rogojski on cuprous sulfites has been largely confirmed by Ramberg.[1] When a current of sulfur dioxide is led into a copper acetate solution, cuprous acetate is first formed and then crystallin $Cu_2SO_3.1/2H_2O$ (colorless). By the action of aqueous sulfurous acid on this hemihydrate, the red monohydrate of Rogojski, $Cu_2SO_3.H_2O$, is formed. If sulfur dioxide is led into an ammoniacal solution of copper sulfate, the colorless anhydrous double sulfite, $(NH_4)_2Cu_2(SO_3)_2$, crystallizes out. In all these preparations care must be taken to exclude all air.

According to Turner when flakes of gold are heated on glass they become transparent. Chapman and Porter[2] find that when heated alone they show no transparency, but that at about 320° the flakes splinter, owing to a contraction, and that it is this splintering into minute particles which, when it takes place on glass, seems to render the gold transparent. On the other hand the finest gold wire shows no sign of contraction, even when heated up to 500°. Grünwald[3] finds that the purple of Cassius consists of a hydrogel of stannic acid colored by colloidal metallic gold.

Group II.—Levi-Malvano[4] has prepared glucinum sulfate hexahydrate in crystals large enough for crystallographical measurement by using a solution of potassium sulfate as solvent. The crystals show no relation to the crystals of the other hexahydrated sulfates of the magnesium series. Parsons and Sargent[5] have reviewed the subject of glucinum compounds with organic acids. Solutions of the normal salts dissolve large amounts of glucinum hydroxide or carbonate, which separates out on dilution. On evaporation, gelatinous or glassy masses are obtained which have no definit composition. The salt with trichloroacetic acid alone crystallizes out as a normal salt (dihydrate) and can be recrystallized from water acidified with trichloroacetic acid.

In a study of Sorel cements, Kallauner[6] finds that in all cases the magnesium chloride can be extracted completely by cold water, and, unless the water in the cement is below 40 per cent., by absolute alcohol. In any case, the alcohol removes a large quantity of the magnesium chloride. The magnesium oxide is only partially converted into the carbonate by carbon dioxide. Kallauner concludes that these cements are to be looked on as solid solutions of magnesium hydroxide and magnesium chloride.

The subject of chemical phosphorescence and luminescence is discussed by Vanino and Zumbusch.[7] The phosphorescence of the alkaline earth sulfides is attributed to the presence of small quantities of polysulfides, the best results being obtained by heating lime with a minimum of sulfur, while the reduction of the sulfate with carbon does not give a phosphorescent mass. The addition of minute traces of heavy metals, as manganese, increases the phosphorescence, but bismuth is far more active in this respect than any metals which have previously been used. Luminescence is often brought out by treatment with hot liquids.

[1] *Z. physik. Chem.*, 69, 512.
[2] *Proc. Roy. Soc. London*, (*A*) 83, 65.
[3] *Sprechsaal*, 43, 419.
[4] *Gazz. chim. ital.*, 39, ii, 438.
[5] THIS JOURNAL, 31, 1202.
[6] *Chem.-Ztg.*, 33, 871.
[7] *J. prakt. Chem.*, [2] 80, 69.

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After many unsuccessful attempts, which are fully described,[1] Glascock has succeeded in preparing metallic strontium in quantity, and its properties are described.

Attempts to prepare metallic radium have apparently met with success in two directions. Madame Curie[2] has electrolyzed a solution of radium chloride, using a mercury cathode. The radium amalgam is very unstable and decomposes water. On distilling it in a current of dry hydrogen most of the mercury distilled at 270°. At 400°, the amalgam was solid and at 700° all the mercury had passed off, and the radium, which fuses at this temperature, began to volatilize. Its vapors attacked the quartz tube very strongly. The metal is silver white, becoming black immediately in the air, owing to the formation of the nitride. It blackens paper, decomposes water energetically and goes into nearly complete solution. As it is much more volatil than barium, sublimation in a vacuum is proposed for its purification. Ebler[3] prepared an azide of barium and radium, $Ra(N_3)_2$, and heated it in a vacuum several hours at 180–250°, obtaining the radium as a metallic mirror. Stock[4], in an investigation of the volatility of the bromides of the alkaline earths in a vacuum, finds that this property is a function of the atomic weight. Thus calcium bromide, $CaBr_2$, sublimes at 720°, strontium bromide at 770° and barium bromide at 820°. Radium bromide seems to require a temperature of about 900°, and this method of separation, or at least enrichment of the barium-radium bromide mixture, is proposed. Working with 0.3942 g. radium bromide, Gray and Ramsay[5] have made a study of the radium emanation. The liquid emanation is colorless and, in glass, phosphorescent. The solid emanation is opaque, fuses at —71°, and shows intense luminosity, varying in color with the temperature. From theoretical considerations its atomic weight would seem to be 176, corresponding to a higher member of the argon group. This would require that radium should also give, on breaking up, a non-active substance of atomic weight 46, or 42 on the supposition that two helium atoms are formed. Using a modification of Bunsen's method, Debierne[6] finds the molecular weight of the emanation to be 220, which is in agreement with the theory that radium breaks up into one atom of helium and one atom of emanation. There is also a place for an element of this atomic weight in the argon group. Later, Ramsay and Gray[7] determined the density of the emanation by actually weighing less than 0.1 cm. on a balance of fused quartz, and as a mean of five experiments find the molecular weight 220, in agreement with Debierne's results. They propose the name of *Niton* for the element. The supposed radioactivity of the alkali salts has continued to attract some attention, but little that is definit has resulted. Henriot[8] decides that potassium gives out β-rays, and that rubidium is twice as active, while lithium, sodium, cesium, and thal-

[1] THIS JOURNAL, 22, 1222.
[2] *Compt. rend.*, 151, 523.
[3] *Ber.*, 43, 2613.
[4] *Ibid.*, 42, 4088.
[5] *J. Chem. Soc.*, 95, 1073.
[6] *Compt. rend.*, 150, 1740.
[7] *Ibid.*, 151, 126.
[8] *Radium*, 7, 40.

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lium show no activity. Elster and Geitel,[1] after efforts to separate some active impurity, conclude that potassium itself is radioactive, as well as rubidium. Büchner,[2] working with the photographic plate, finds an undoubted blackening in the presence of rubidium salts, but none with any of the other alkalies. The rubidium activity passes through aluminium foil, but is greatly weakened. After working up several tons of pitchblende, Madame Curie and Debierne[3] have obtained the polonium present concentrated in 2 mg. of substance, which contain about 0.1 mg. of actual polonium. Its spectrum and some of its properties have been studied. Among the gases given off from its solution, helium was found in nearly theoretical quantity.

If a test tube is partly filled with barium amalgam and closed with a rubber stopper, in the course of time the under edge of the stopper shows a black ring, which proves to be carbon. As other amalgams show the same phenomenon, von Bolton[4] ascribes it to the vapors of mercury. Other carbon compounds, such as $CHCl_3$, CS_2, and CO_2, are similarly decomposed with the deposition of carbon. In the case of caoutchouc the carbon showed minute crystals, which appear to be diamond. von Bolton suggests that the formation of (inorganic) graphite and diamond in nature may be due to the action of metallic vapors on CO_2.

Group III.—In the attempted preparation of crystallized boron by the Goldschmidt process, using boric oxide, aluminium filings and sulfur, in addition to the black crystals of AlB_{12}, the lighter colored transparent crystals first described by Wöhler were in no case obtained by Biltz.[5] These crystals, to which Hampe assigned the formula $C_2Al_3B_{48}$, were readily obtained when carbon or aluminium carbide was added to the mixture, and were separated from the slightly lighter black crystals by floating in methylene iodide-benzene solution. This quadratic boron, called by Wöhler "diamond boron," is not attacked by concentrated sulfuric acid with chromic acid, but is slowly acted on by boiling concentrated nitric acid. The formula is $C_2Al_3B_{44}$, but in spite of the constancy of the carbon-aluminium ratio it is very doubtful if the crystals are a definit chemical compound.

Verneuil[6] has prepared sapphires in the oxyhydrogen blowpipe by adding iron oxide and titanic acid to the alumina. The best color was obtained when 1.5 per cent. Fe_3O_4 and 0.5 per cent. TiO_2 were used. Crystallographically true sapphire was formed, although Deville and Caron attribute the color of natural sapphires to the presence of a lower oxide of chromium.

In continuing his work on scandium, Crookes[7] has prepared a large number of new salts, many of them with organic acids. A considerable number of these are basic. Meyer and Winter[8] have also continued their

[1] *Physik. Z.*, 11, 2750.
[2] *K. Akad. Wetenschappen*, 18, 91.
[3] *Radium*, 7, 38.
[4] *Z. Elektrochem.*, 16, 667.
[5] *Ber.*, 43, 297.
[6] *Compt. rend.*, 150, 185.
[7] *Proc. Roy. Soc. London*, (*A*) 84, 79.
[8] *Z. anorg. Chem.*, 67, 398.

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work on scandium, and their paper deals with its preparation and purification. It is readily separated from all the earths except thorium. The nearly insoluble scandium iodate offers a satisfactory means of separation, but boiling with a saturated solution of sodium carbonate is even better, a nearly insoluble double carbonate, $4Na_2CO_3.Sc_2(CO_3)_3.6H_2O$, being precipitated. Further spectroscopic examination of rocks and minerals by Eberhard[1] confirms the exceedingly wide distribution of the element. All the minerals in which it can be detected chemically, however, have their origin in granits and pegmatites.

In continuing his work upon the bromates of the rare earths, James (and Langelier)[2] describe the properties of the bromates of lanthanum, cerium, praseodymium, neodymium, and yttrium, which are best prepared by action of the sulfates on barium bromate, and which have the formula $M_2(BrO_3)_6.18H_2O$. James and Pratt[3] have studied the system $Y_2O_3.N_2O_5.H_2O$, and find one definit basic yttrium nitrate, $3Y_2O_3.4N_2O_5.20H_2O$. The priority contest regarding the splitting of ytterbium continues to call forth articles, but the names given by Urbain, lutecium and neoytterbium, seem to receive more favor than the aldebaranium and cassiopeium of Auer von Welsbach. Thiele has continued his researches on indium.[4] He finds In_2O_3 stable up to about 1000° but above this it is slowly decomposed, and in one experiment he obtaineed In_3O_4, in regular crystals, possibly corresponding to magnetite. InI_3 and InI were prepared synthetically, and evidence of the existence of InI_2 was obtained from the fusing-point curve of their mixture. The three sulfides, In_2S, InS and In_2S_3, all exist as well as In_2Se_3 and InTe.

Group IV.—The action of carbon tetrachloride on metallic oxides has been studied by Camboulives,[5] both with reference to the compound formed and the temperature at which the reaction begins. Fe_2O_3 is attacked as low as 245° while WO_3 requires 560°. In general the chloride is formed but tungsten gives the oxychloride and columbium and thorium, mixtures of the chloride and oxychloride. The chloride formed generally corresponds in valence to the oxide, but V_2O_5 gives VCl_4, MoO_3 gives $MoCl_5$, and UO_3 a mixture of UCl_4 and UCl_5. For Cr, Ni, V, Ti, Zr, Gl and especially for the rare earths the method is an excellent one for the preparation of the chlorides. Some minerals, as corundum and beryl, are but little acted on, and silica is not attacked. The method is available for quantitative separation of SiO_2, since this is not affected. Thus the aluminium silicate in clay is volatilized as $AlCl_3$ and $SiCl_4$, while the free silica and sand are not acted on. Work on metallic carbonyls, upon which Ludwig Mond was engaged at the time of his death, has been published by his son.[6] Carbonyls of nickel, cobalt, iron, molybdenum and ruthenium have been made, except in the case of nickel, by the use of high pressures. The $Co(CO)_4$ consists of orange crystals with a very low vapor pressure. At 50°–60°, it decomposes into $Co(CO)_3$ and CO. $Fe(CO)_5$, a yellow liquid with considerable vapor pressure, is decomposed in the

[1] *Sitzb. kg. preuss. Akad. Wiss.*, 1910, 404.
[2] THIS JOURNAL, 31, 913.
[3] *Ibid.*, 32, 873.
[4] *Z. anorg. Chem.*, 66, 288.
[5] *Compt. rend.*, 150, 175, 221.
[6] *J. Chem. Soc.*, 97, 798.

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light, $Fe_2(CO)_9$ being formed, and this when heated in solution to 95° becomes $Fe(CO)_4$. $Mo(CO)_6$ consists of white crystals. A carbonyl of ruthenium was formed as an orange-red deposit in very small quantity when the metal was heated to 300° at 350–450 atmospheres. No carbonyls of chromium, manganese, tungsten, palladium or rhodium were obtained, even at extreme pressures. No evidence of any carbonyl of nickel other than $Ni(CO)_4$ was found. As regards constitution, direct combination of the carbonyl groups with the metal seems contradictory to our ideas of valence, and there seems to be no probability that the carbon atoms form a ring, especially since the cobalt carbonyl has the formula $Co_2(CO)_8$ in solution while the formula of nickel carbonyl is $Ni(CO)_4$, nor can the nonacarbonyl of iron be brought into line from the standpoint of a carbon ring. It seems probable that these compounds have a "molecular" composition, the carbonyl group being somewhat similar to water of crystallization or hydration, though on this hypothesis it is difficult to explain the normal gas density of several.

Hönigschmid has investigated the silicides of the alkaline earths.[1] Technical calcium silicide with 30 per cent. calcium contains $CaSi_2$, with free silicon and some iron silicide. The 60 per cent. silicide contains some $CaSi_2$, but consists chiefly of Ca_3Si_2, and approaches metallic calcium in its properties. The technical magnesium silicide consists of Mg_2Si and free silicon. When free silicon is present the color is bright blue. On decomposition with fuming hydrochloric acid, $CaSi_2$ gives a silicone of composition $Si_3H_3O_2$, which was discovered by Wöhler. This is dark yellow, but instantly becomes white on exposure to sunlight, through oxidation. On heating in a vacuum it leaves a residue which is probably Si_3O_2. The white silicone, Wöhler's leucone, on similar heating leaves a brownish-yellow residue, apparently a new oxide, Si_3O_4. Kolb,[2] by fusing together in hydrogen calcium and pure silicon, obtains two silicides to which he assigns the formulas Ca_6Si_{10} and $Ca_{12}Si_{10}$. From each of these a silicone is obtained. Both silicides absorb nitrogen readily, the former giving a mixture of $CaSi_2N_3$ and $Ca_2Si_3N_4$, and the latter giving $Ca_{11}Si_{10}N_{10}$.

Attempts to obtain metallic titanium by the reduction of the fluorotitanates were found by Hunter[3] to give a product containing at best 73 per cent. of the metal. The reduction of TiO_2 by carbon in a vacuum likewise gave an impure product. The reduction of pure $TiCl_4$ by metallic sodium in a steel cylinder proved more successful, the product being partly a powder, but with some completely fused material which was pure titanium. The metal looks like polished steel, and is hard and brittle, but can be worked at a dark red heat. It burns in the air at 1200°, and fuses at 1800°–1850°. Its specific gravity is 4.50. Weiss and Kaiser[4] also have studied metallic titanium, using the fluorotitanate method to prepare it. Their product seems to have been less pure than that of Hunter.

Two investigations on metallic zirconium have appeared, one by Weiss[5]

[1] *Monatsh.*, 30, 497, 509.
[2] *Z. anorg. Chem.*, 64, 342.
[3] THIS JOURNAL, 32, 330.
[4] *Z. anorg. Chem.*, 65, 345.
[5] *Ibid.*, 65, 178, 248.

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and the other by Wedekind[1]. Weiss' source of zirconia was a Brazilian dioxide "Zircon-Favas," which, though microcrystallin, seems to be isomorphous with rutile and cassiterite. The metallic zirconium was obtained by the reduction of the fluo-zirconate by sodium, and also by aluminium, the aluminium being finally removed by volatilization in an electric vacuum furnace. Wedekind used the former method, but did not get so pure a zirconium. That of Weiss was obtained in fused globules. The density of the pure metal is 6.4, its melting point 2350°. Zirconium hydride, ZrH_2, is formed when powdered zirconium is heated in hydrogen. When the hydride is heated in oxygen it burns, forming a new greenish-white oxide, Zr_2O_3, which is very stable and is but slowly oxidized to ZrO_2 by heating in the air.

Group V.—In the course of attempts to prepare compounds of argon (later referred to), Fischer and Schröter[2] have obtained nitrides of most of the metals, many of them never before described, as those of Na, K, Rb, Cd, In, Tl, Pb, As, Sb, Te. By heating the element in an atmosphere of nitrogen in the electric arc and cooling the products by a mixture of liquid argon and nitrogen, it was possible to prepare nitrides of all the metals of the second series of each periodic group, even the very unstable nitrides such as those of mercury, thallium, lead and bismuth. All were found to be derivatives of NH_3, no trace of derivatives of N_2H_4 or any other N-H compounds being found. The nitrides of elements of high atomic weight, as mercury, lead, and bismuth, explode on being allowed to come to ordinary temperature, while the others decompose more quietly. Only the elements of the first series of each periodic group form nitrides which are stable at ordinary temperature. The authors suggest the hypothesis that when the atmosphere of the earth was at a temperature of several thousand degrees, at least a part of the nitrogen was present in the form of these endothermic nitrides, which have been gradually decomposed as the earth has cooled. Wolk[3] finds the most favorable temperature for the formation of aluminium nitride, AlN, by heating finely divided aluminium in nitrogen, is 820–850°. Below 700° no action takes place, while at higher temperatures the product sinters together and has no longer a uniform composition. The lower the temperature of formation the more readily does the nitride decompose in water. The nitrogen compounds with silicon have been studied by Weiss.[4] The silicon was heated in a current of nitrogen. The absorption of nitrogen was slow, the most favorable temperature being 1240°–1300°. According to different treatments of the resultant mass, the silicides SiN, Si_3N_4, and Si_2N_3 were obtained. All are white amorphous solids, very resistant to chemical action. When silicon is heated in the presence of carbon, nitrogen is absorbed and a carbonitride, Si_3C_3N, formed. This is probably identical with the similar product to which Schützenberger assigned the formula Si_2C_2N.

Zinc hydrazide has been prepared by Ebler and Krause[5] by the action of dry hydrazine on zinc ethide in dry ether and in a nitrogen atmos-

[1] *Ann.*, 371, 366.
[2] *Ber.*, 43, 1465.
[3] *Compt. rend.*, 151, 318.
[4] *Z. anorg. Chem.*, 65, 38.
[5] *Ber.*, 43, 1690.

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phere, and also by the action of hydrazine on zinc amide. The hydrazide takes fire spontaneously in the air. Hydrazides of other metals can be prepared by a similar reaction. The dry hydrazine was prepared by Ebler by the prolonged action of barium hydroxide on hydrazine hydrate, while Raschig[1] advises the use of caustic soda.

A complete summary of his work on the metal-ammonia bases, containing more than one atom of the metal in the nucleus, is given by Werner,[2] together with the bearing of the work on his theory of the constitution of these bases. The metal atoms (Co) in the nucleus may be united not only by an oxygen atom, but also by NH_2, NH, OH, OH_2, O_2, and further by certain acid radicals such as NO_2, SO_4, and $OCO.CH_3$. Altogether 23 different complex nuclei have been recognized, which are fully described and discussed in the paper. Werner has further, partially in conjunction with Riesenfeld,[3] described a number of new aquochromium-triammine salts, which show many correspondences with the cobalt salts of similar constitution. They are all derived from the chromium triammine tetraoxide, which is readily prepared by the action of concentrated ammonia on pyridine perchromate, the latter being formed from chromic acid, pyridine and hydrogen peroxide. The aberrant results obtained in the determination of hydroxylamine with copper sulfate, according to concentration and temperature, have been investigated by Adams and Overman,[4] who find the existence of several intermediate compounds, which have been isolated. These are $CuSO_4.NH_2OH$, $CuSO_4.2NH_2OH$, $CuSO_4.3NH_2OH$ and $Cu_2O.SO_4.2NH_2OH$. When heated with excess of hydroxylamine in the presence of NaOH the reduction to metallic copper is complete. The reaction between ammonium chloride and potassium dichromate has been found by Frankforter, Roehrich and Manuel[5] to be very complex, the evolved gas containing not merely nitrogen as assumed by Ramon de Luna, but also nitric oxide and even nitrogen dioxide. In one case as much as 45 per cent. NO was obtained. The composition of the residue also depends upon the composition of the original mixture. The complexity of the reaction is attributed to the fact that the ammonium chloride dissociates into ammonia and hydrogen chloride, and the former diffuses out of the mixture more rapidly than the latter.

Hayhurst and Pring[6] have examined the atmosphere at different elevations for the presence of nitrogen oxides and ozone, by passing the air through a perfectly neutral solution of potassium iodide, and determining the liberated iodine, the free alkali and the iodate formed. They find that at low and at moderate elevations the amount of nitrogen oxides is very variable and that the amount of ozone is not sufficient to determin, at all events less than 0.003 mg. per 10 cu. m. At the height of 10 miles small amounts of ozone are found, 0.04 mg. in from 0.1 to 0.3 cu. m. The amount of nitrogen oxides is here less than the amount of ozone. Adwentowski[7] has studied nitric oxide at low temperatures,

[1] *Ber.*, 43, 1927.
[2] *Ann.*, 375, 1.
[3] *Ber.*, 42, 4222; 43, 2286.
[4] This Journal, 31, 637.
[5] *Ibid.*, 32, 178.
[6] *J. Chem. Soc.*, 97, 868.
[7] *Anz. Akad. Wiss. Krakau*, 1909, 742.

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and from the vapor-pressure curve concludes that at high pressures the gas is somewhat polymerized. It is, however, completely dissociated at atmospheric pressure. The melting point of the solid NO is —160.6° with a pressure of 168 mm. The boiling point at 760 mm. is —150.2°, the critical temperature —92.9° and the critical pressure 49,095 mm. The bluish color of the solid and liquid is attributed to the presence of a little N_2O_3, which it is impossible to remove. Numerous articles by Haber and his colleagues have appeared in Vol. 16 of the *Z. Elektrochem.* on the formation of the oxides of nitrogen from the atmosphere in the electric arc under various conditions, and Guye has reviewed the whole subject critically in the *Bull. soc. chim.*, [4] **5**, No. 20. The papers are of great interest in connection with the rapidly developing synthetic nitrate industry, but do not admit of abstraction. Guntz and Martin[1] have prepared the anhydrous nitrates of manganese, nickel, cobalt and copper by the use of N_2O_5 in a vacuum for the removal of the last of the water of crystallization. By the action of metals on $AgNO_3$ in non-aqueous solvents, the nitrates of the above metals are obtained, combined with the solvent, as $5Cu(NO_3)_2.4CH_3COCH_3$ and $2Mn(NO_3)_2.C_6H_5CN$. In liquid ammonia, $Mn(NO_3)_2.9NH_3$ was obtained and analogous compounds of nickel and cobalt. With copper, $Cu(NO_3)_2.7NH_3$ was formed, which in a vacuum became $Cu(NO_3)_2.4NH_3$.

Several papers on elementary phosphorus have appeared during the past year, whose results are not in complete agreement. Gernez[2] has examined the coating which appears on ordinary yellow phosphorus when kept under water. This coating is white when formed in the dark but yellow to red when exposed to the light. In both cases, however, it is composed of ordinary yellow phosphorus. Phosphorus oxidizes slightly under water and the oxide formed dissolves in the water leaving the surface covered with phosphorus in minute flakes which causes the opaque appearance. According to Jolibois[3] the red phosphorus of commerce can be separated into larger dark violet and smaller yellowish red particles, but the violet are changed into the yellowish red by rubbing and are not a distinct modification. If the violet particles are heated out of access of air to 400° they pass slowly into a new modification, which Jolibois calls red pyromorphic phosphorus. The change takes place rapidly at 600°, and it is also accelerated by the presence of iodine. This modification has a density of 2.37 and is a definit allotropic form. On the other hand, Cohen[4] finds only two modifications of phosphorus, the ordinary yellow and the "metallic" or Hittorf's phosphorus. The red or amorphous phosphorus of trade is a solid solution of yellow phosphorus in metallic phosphorus. The composition of this solid solution is a function of the temperature. The so-called constants of red phosphorus found in its literature have no value. Stock[5] has made a very complete study of the metallic phosphorus, which also according to him is the only modification of phosphorus except the ordinary yellow form. The metallic phosphorus is best prepared by dissolving phosphorus in metallic lead

[1] *Bull. soc. chim.*, [4] 5, 1004; 7, 313.
[2] *Ann. chim. phys.*, [8] 21, 5.
[3] *Compt. rend.*, 149, 287.
[4] *Z. physik. Chem.*, 71, 1.
[5] *Ber.*, 42, 4510.

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and separating the lead by anodic solution in an acetic acid solution of lead acetate. By using 100 grams lead and 1.5 grams of phosphorus, about 0.5 gram metallic phosphorus can be obtained. Bismuth can be substituted for lead, and while better crystals are obtained the output is smaller. It can also be prepared with difficulty by sublimation. Under the microscope the metallic phosphorus is seen to consist of yellow to brown, more or less transparent tables, with some acicular crystals. They contain small quantities of lead (or bismuth), apparently in solid solution. While ordinary yellow phosphorus unites slowly with sulfur to form phosphorus sulfide, the metallic phosphorus hardly reacts with sulfur. It oxidizes slowly in the air, and that formed by sublimation oxidizes as soon as the tube in which it was formed is opened. [The nomenclature of phosphorus is much in need of revision. We now have "common," "white" or "yellow" phosphorus; "red "or "amorphous;" and "metallic," "crystallin," "violet," or "Hittorf's" phosphorus; and not one of these names is wholly satisfactory.—REVIEWER.] Gernez[1] has also examined the so-called "black" phosphorus discovered by Thénard in 1812. When mercury is dissolved in phosphorus the solution is colorless and if saturated or supersaturated, it remains colorless. When it crystallizes the mercury separates out and colors the mass intense black. The mercury is then so finely divided that, on warming, the fused phosphorus immediately redissolves the mercury again to a colorless solution. Stock[2] has continued his work on the sulfides of phosphorus, completing his description of the properties of P_4S_7, and also of P_4S_{10}, which has not before been obtained in a pure condition. The latter boils at 513°–515° with some decomposition, and at 600° its density corresponds to the formula P_2S_5. It is interesting to note that as regards color, specific gravity, melting and boiling points, solubility and stability, P_4S_7, so far from standing intermediate between P_4S_3 and P_4S_{10}, lies entirely outside the other two. This much simplifies the problem which Stock has before him of investigating other sulfides of phosphorus, which he feels certain exist. By submitting a mixture of phosphorus trichloride and hydrogen to the action of an electric discharge, Besson and Fournier[3] obtained the dichloride, P_2Cl_4, a colorless oil, solidifying at low temperatures to a white mass, which fuses at —28°. In the presence of an indifferent gas it boils at 180° with slight decomposition. The compound is rather unstable and gives decomposition products which have not yet been investigated. Zhemchuzhnuii and Shepelev,[4] prepare metallic phosphides by mixing the finely divided metal with red phosphorus and throwing the mixture in small lumps into a hot crucible. Some of the phosphorus burns while the rest unites with the metal. The melt is covered with a protecting layer of barium chloride and the temperature raised. Red phosphorus is then added in asbestos capsules, and more metal and phosphorus as desired. The mass is then investigated as an alloy. In this way but a single phosphide of cobalt is found to exist, Co_2P, which, however, is found in two distinct modifications.

[1] *Compt. rend.*, 151, 12.
[2] *Ber.*, 43, 414, 1223.
[3] *Compt. rend.*, 150, 102.
[4] *Z. anorg. Chem.*, 64, 245.

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The action of phosphorous and hypophosphorous acids on metallic salts has been studied by Sieverts,[1] who finds that cupric salts alone are reduced to a hydride by hypophosphorous acid. The oxidation of the acid to phosphorous acid corresponds to the accepted formula, CuH. Phosphorous acid reduces copper sulfate to metallic copper. Cupric chloride is reduced by both acids to cuprous chloride. Gold and silver salts are reduced by both acids to the metal and the same is true of palladium, while platinum chloride is not affected, nor are the salts of nickel and cobalt. More work has been done on hypophosphoric acid by Cornec,[2] who proposes as a better method of preparation, placing sticks of phosphorus between glass rods on the corrugated bottom of a developing tray, and partly covering with water. The tray is covered with a glass plate, and by putting ice on this the temperature can be controlled, if necessary. From cryoscopic determinations of the acid and its salts, Cornec inclines to the formula $H_4P_2O_6$, though the esters seem to have the simpler formula. Rosenheim[3] prepares hypophosphoric acid by a modification of a process proposed by Cornec, allowing yellow phosphorus to react with a solution of copper nitrate containing considerable nitric acid. The copper nitrate can be replaced by silver nitrate, but not by the nitrates of other metals, since the catalytic action of the copper or silver seems to be necessary. Good results were also obtained by the anodic oxidation of copper phosphide, while iron phosphide gave only phosphoric acid. The hypophosphoric acid is separated as the acid sodium salt, $NaHPO_3.2H_2O$, which is but slightly soluble. Guanidine carbonate is the best reagent for the detection of hypophosphates, forming a very slightly soluble salt, $(CN_3H_5)_4.H_2PO_3.5H_2O$. By this means it may be detected in mixtures of other phosphorous acids. The boiling point determinations of benzylhypophosphate in ether confirmed the results previously obtained with the methyl and ethyl esters and indicate the simpler formula as correct. The same was true of conductivity determinations of the acid. Rosenheim concludes that while the formula of the acid is H_2PO_3, it has a strong tendency to association in aqueous solutions, which accounts for the results obtained which seem to point to the formula $H_4P_2O_6$. Schmidlin and Massini[4] have prepared by the action of phosphorus pentoxide on hydrogen peroxide a phosphorus "monoper acid" analogous to the Caro acid, and possessing similar properties. Its formula is H_3PO_5. If sirupy pyrophosphoric acid in large excess acts on hydrogen peroxide, a perphosphoric acid is formed which from analogy has the formula $H_4P_2O_8$. Several hundred crystals of struvite are recorded by Böggild as having[5] been found in a well 10 to 35 meters deep, on Limfjord. The deposit contained many shells of mollusks and vegetable remains. The crystals were from 1 to 5 cm. in diameter and 1 to 5 mm. in thickness. Ephraim[6] has prepared barium and magnesium mono-oxy-trithiophosphates and barium dioxydithiophosphate ($Ba_3(PS_3O)_2.20H_2O$ and $Ba_3(PS_2O_2)_2.18H_2O$) by the restrained

[1] *Z. anorg. Chem.*, 64, 29.
[2] *Bull. soc. chim.*, [4] 5, 1058, 1081, 1121.
[3] *Ber.*, 43, 2003.
[4] *Ibid.*, 43, 1162.
[5] *Neues Jahrb. Min. Geol.*, 1910, i, 335.
[6] *Ber.*, 43, 285.

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action of barium (or magnesium) sulfide on sodium (tetra) thiophosphate. He has also prepared[1] a number of oxy-selenophosphates, but apparently the mono-oxytriseleno- and dioxydiselenophosphates form isomorphous mixtures. It was not found possible to prepare the tetraselenophosphates in solid form.

Steel describes[2] a deposit of feathery plates of pearly white luster of $As_2O_3.SO_3$ found in the iron sight tubes of a sulfur burner at Clyde, New South Wales. The burners used Japanese sulfur with a content of about 0.005 per cent. arsenic. The crystals were very hygroscopic and instantly decomposed by water. Ephraim has repeated[3] the work of Gibbs on the arseno-molybdates and fails to obtain any of the compounds made by Gibbs which had 3 : 5 : 12 : 24 and 3 : 2 : 8 : 13 ratios, but has prepared salts of potassium with 3 : 1 : 5 : 3 and 3 : 1 : 8 : 18 ratios, and sodium salts with 1 : 1 : 2 : 6 and 2 : 1 : 4 : 13 ratios, as well as ammonium barium and ammonium copper salts.

A new type of compounds is described by Ruff,[4] containing SbF_5 and $SbCl_5$ in the ratios 3 : 1, 2 : 1, 1 : 1, 2 : 3, 1 : 2, and 1 : 3. These are formed by direct mixture or by the action of chlorine on a mixture of SbF_3 and $SbCl_5$. They seem to be definit compounds, and the two constituents of the compounds are considered by Ruff as acting as elements, the affinity of SbF_5 lying between that of fluorine and chlorine while that of $SbCl_5$ is as strong as that of bromine. The affinity between the two constituents may be therefore considered as equal to that existing between fluorine and bromine, or between chlorine and iodine. He likens these compounds to such as $AgI.AgNO_3$ and $CaF_2.CaCl_2$. Ephraim[5] has made a study of the double halides of quadrivalent antimony, and concludes that the equilibrium $SbCl_3 + SbCl_5 \rightleftarrows 2SbCl_4$ is to a great extent dependent on the temperature and the possibility of ionization. He has also prepared triple salts containing $FeCl_3$ with quadrivalent antimony, and a number of salts of the alkylammonium halides, with trivalent and with quinquivalent antimony.

The solubility of bismuth sulfide in alkali sulfides and bismuth oxide in the alkalies has been re-investigated by Knox,[6] who finds that the sulfide is somewhat soluble in K_2S and Na_2S, the solubility increasing nearly proportionally to the third power of the concentration. This is accounted for by assuming the existence of a thio-bismuthic anion. The sulfide is insoluble in the hydrosulfides and in the higher polysulfides. In the disulfide it is only one-third as soluble as in the monosulfide. In ammonium sulfides it is practically insoluble. A slight solubility was found for bismuth oxide in sodium hydroxide. These results correspond to the position of bismuth in the periodic table.

Prandtl and Bleyer[7] have tried to prepare pure metallic vanadium by reduction of the pentoxide with aluminium or calcium-aluminium by the Goldschmidt process. The best results are obtained by using a

[1] *Ber.*, 43, 277.
[2] *J. Soc. Chem. Ind.*, 29, 1142.
[3] *Z. anorg. Chem.*, 66, 53.
[4] *Ber.*, 42, 4021.
[5] *Ibid.*, 4447.
[6] *J. Chem. Soc.*, 95, 1760.
[7] *Z. anorg. Chem.*, 64, 217. *Ber.*, 43, 2602.

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fluorspar lining for the crucible or by adding fluorspar to the mixture, but in no case was a vanadium more than 95 per cent. pure obtained. As the ordinary impurities were absent, the result can only be accounted for by the presence of a lower oxide of vanadium, which alloys itself with an excess of the metal and so is protected from the action of the reducing agent.

A long paper by Weiss and Landecker[1] has appeared on the preparation and separation of columbic and tantalic acids, in which they describe critically the action of many reagents and methods of separation. To separate the metals they prefer to fuse with sodium carbonate and a minimum of saltpeter. The columbate melt is easily soluble in water and not precipitated by CO_2, while the tantalate melt is far less soluble and is precipitated by CO_2. Hence they warm the melt with very little water and wash the tantalate residue with sodium bicarbonate solution. Any columbate that goes into solution is precipitated by CO_2 and brief boiling. The tantalate residue is free from columbic acid, and is dissolved in sulfuric acid with the addition of hydrogen peroxide, from which the tantalum is precipitated by SO_2. If care is used as to temperatures and quantities of reagents, they claim that the separation is practically complete. The investigation of the halides of tantalum at the University of Pennsylvania laboratory has been continued.[2] Chapin applied the process by which Chabrié obtained the dichloride, $TaCl_2.2H_2O$, to the bromide, heating the pentabromide with sodium amalgam in a vacuum. The bromide obtained has the formula $Ta_6Br_{14}.7H_2O$. While the dichloride is green, this bromide is black, but gives a dark green powder in a mortar. Its solution is almost opaque. Only two atoms of bromine are precipitated by silver nitrate, and these may be replaced by other negative radicals, so that Ta_6Br_{12} proves to act as a bivalent base. A re-investigation of Chabrié's chloride shows that it also has a complex formula, being really $Ta_6Cl_{12}.Cl_2.2H_2O$, analogous to that of the bromide. Van Haagen finds that $TaBr_5$ is readily formed by heating the oxide with carbon in a current of dry bromine, fuses at 240° and boils at 320°. It dissolves in absolute methyl and ethyl alcohols with which it seems to form esters. Lower bromides, except the one described above, could not be prepared. The pentaiodide was made by distilling the bromide repeatedly in a current of hydrogen iodide. No oxy-iodide was found. Biltz[3] has prepared the sulfide of tantalum, which has the formula TaS_2, by heating the oxide in a stream of H_2S saturated with carbon disulfide. The reaction begins at 650° but is not complete at 900°. The sulfide is stable up to at least 1300°, but is hygroscopic and decomposes in warm, moist air. Biltz conjectures that the formula for the sulfide of columbium should also be CbS_2.

Group VI.—In connection with his work on the conditions of existence of matter,[4] von Veimarn describes the preparation of colloidal ice[5] by the sudden cooling in liquid air of saturated solutions of numerous salts, such as various thiocyanates, calcium chloride, aluminium sulfate, ferric

[1] *Z. anorg. Chem.*, 64, 65.
[2] THIS JOURNAL, 32, 323, 729.
[3] *Ber.*, 43, 1636.
[4] *Z. Chem. Ind. Kolloide*, 3, 282.
[5] *J. Russ. Phys. Chem. Soc.*, 42, 65, 69.

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chloride, etc. In this way are formed completely transparent and stable glasses which contain solid solutions of ice. By adding small quantities of water to liquid air the water assumes in part a semi-solid condition, while by adding drops of liquid air to water the drops become covered with an elastic ice membrane. Wolfgang Ostwald[1] discusses the subject fully and describes colloidal ice solutions obtained by cooling dilute solutions of water in organic solvents such as toluene, xylene, etc. These solutions may be made more stable by the addition of protective colloids as mastic, or the aluminium salts of the fatty acids. They have a yellowish blue fluorescence and pass unchanged through the finest filter paper.

Jones has continued his work on hydrates in solution,[2] with especial reference to the temperature coefficient of conductivity, and finds further confirmation of the theory that the change in conductivity with the temperature is largely due to the decrease in complexity of the hydrates. The water of crystallization of many salts has been studied by Masson[3] by mixing with calcium carbide, and collecting the evolved acetylene over mercury. $ZnSO_4.7H_2O$, for example, loses five molecules of water in the cold, and one further molecule at 100°. Ammonium iron alum goes over in the cold into the trihydrate and at 145° into the monohydrate. Ammonium aluminium alum and common alum lose 10.5 molecules of water at 130°–160°, etc.

By pouring liquid sulfur at 400° into liquid air, von Veimarn[4] obtains threads of sulfur which are hard and brittle but which when the temperature rises become remarkably elastic. At ordinary temperature they pass rapidly into common plastic sulfur. He regards sulfur as presenting an especially good example of the tendency of those substances which can exist in numerous modifications to give most readily colloidal forms. Gardner and Hodgson[5] have investigated the tendency of wool, dyed with sulfur blacks, to deteriorate, especially in warm climates. They find that by boiling with ether it is possible to extract considerable quantities of sulfur from the dyes, alone, or on the fiber, and it is the ready oxidation of this finely divided sulfur that weakens the wool. No dyeing procedure obviates this difficulty, which proceeds from the decomposition of the dyestuff itself, in which the sulfur seems to be loosely combined. They find also that from "pure" antimony sulfide of commerce upwards of 35 per cent. of sulfur can be extracted by ether in 24 hours. This is quite in line with investigations of Jordis[6] on sulfides, in which he finds that sulfur can be more or less readily extracted, and this, whether working on sulfides formed by precipitation or by fusion. The conclusion is that sulfides, while definit in composition, nevertheless have their sulfur somewhat loosely combined, and it is given up to solvents more or less easily. Precipitated sulfides are, however, often if not generally, of indefinit composition. The ready formation of sulfuric acid in precipitated sulfides is not due solely to free sulfur which may be present, but to sulfur liberated from the sulfides.

[1] *Z. Chem. Ind. Kolloide*, 6, 183.
[2] *Am. Chem. J.*, 43, 187.
[3] *J. Chem. Soc.*, 97, 851.
[4] *Z. Chem. Ind. Kolloide*, 6, 250.
[5] *J. Soc. Chem. Ind.*, 29, 672.
[6] *Z. angew. Chem.*, 23, 577.

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The stability and decomposition products of silver sulfite have been studied by Baubigny.[1] Contrary to the ordinarily accepted view that in boiling water the sulfite decomposes into silver sulfate and metallic silver, he finds that silver dithionate is the principal product of the decomposition. Only at higher temperatures, as 200°, are any considerable quantities of sulfate and SO_2 formed, and these come from the decomposition of the dithionate. The same is true even when the alkali sulfite is in large excess. Precipitated silver sulfite has the normal formula Ag_2SO_3, and is scarcely soluble in water (less than 1 : 20,000). In the dark the precipitate is stable, but gradually darkens in the light. To determin the dithionic acid the evaporated solution is heated with sodium carbonate and saltpeter, since neither aqua regia nor bromine oxidize it completely to the sulfate. This decomposition confirms the formula $H_2S_2O_6$ (and not HSO_3 as held by Kolbe). It also furnishes a new argument for the asymmetrical formula, $H.SO_2.OH$, since in the silver salt the two silver atoms act differently. It agrees also with the asymmetrical formula for thiosulfuric acid, $HS.SO_2.OH$. According to this view, dithionic acid is to be looked on as disulfonic acid, $HO_3S.SO_3H$, sulfurous acid as hydrogen monosulfonic acid, $H.SO_3H$, thiosulfuric acid as the monosulfonic acid of hydrogen sulfide, $HS.SO_3H$, and benzene sulfonic acid as the monosulfonic acid of phenyl, $C_6H_5.SO_3H$. The last is monobasic, while sulfurous and thiosulfuric acids are dibasic, since in these latter there is retained a typical hydrogen atom of the original H_2 and H_2S molecule. The reaction between sulfuryl chloride and ammonia, first studied by Traube and Hantzsch, has been further investigated by Ephraim and Michel.[2] Instead of the expected sulfamide, $SO_2(NH_2)_2$, a series of much more complicated imides is formed whose formulas can be expressed by $NH_2.(SO_2.NH)_x.SO_2.NH_2$. These compounds give silver salts in which the hydrogen is partly or completely replaced by silver. In other efforts to prepare sulfamide, the chloroamide of sulfuric acid, $ClSO_2.NH_2$, and the ammonium salt of chlorosulfuric acid, $ClSO_2.ONH_4$, were formed, both hitherto undescribed. The best results in the preparation of sulfamide were obtained by the method proposed by Ruff, where sulfuryl chloride is slowly dropped into liquid ammonia. A mixture of the ammonium salt of imidosulfamide, $NH.(SO_2.NH_2)_2$, and ammonium chloride is first obtained, which after acidification is gently evaporated to dryness. The ammonium imidosulfamide is converted by hydrolysis into amino sulfuric acid and sulfamide, the latter being extracted by dry acetic ester, from which it crystallizes in great purity.

Pellini[3] finds but one compound of mercury and selenium, HgSe, which is formed slowly and in an impure condition by rubbing the elements together in a mortar, but better by heating molecular quantities under pressure to 550°–600°, or by heating mercury with an excess of selenium at ordinary pressure. By rubbing together mercury and tellurium, the telluride, HgTe, is formed more readily than the selenide, but the compound is less stable and decomposes in a vacuum at 370°. According to Olivari[4] the molecule of selenium in fused $HgCl_2$ solution varies from

[1] *Compt. rend.*, 149, 735, 858; 150, 973. *Bull. soc. chim.*, [4] 7, 4, 51.
[2] *Ber.*, 42, 3833; 43, 138.
[3] *Atti accad. Lincei, Rome*, [5] 18, ii, 211.
[4] *Ibid.*, 94.

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Se_2 to Se_4 when the solution is dilute, but in more concentrated solutions tends toward Se_8. In similar solution the S_8 molecule shows greater stability. Tellurium, when heated with mercuric chloride, reacts, with the formation of HgCl and $TeCl_2$. Investigation by Beckmann[1] renders the existence of $SeCl_2$ highly improbable, the only two chlorides of selenium being Se_2Cl_2 and $SeCl_4$. Unlike the case with sulfur, $SeCl_4$ is by far the most stable. With bromine and selenium are formed mixtures of Se_2Br_2 and $SeBr_4$ but no $SeBr_2$. While boiling point determinations show the molecule of sulfur in bromine is S_2, selenium has under the same conditions a monoatomic molecule. When aqueous solutions of KSeCN and $HgCl_2$ react in the proportion of 2 : 1, Rosenheim and Pritze[2] find that $Hg(SeCN)_2$ is precipitated in white needles, which are decomposed by hot water with the separation of selenium. If the proportion is 1 : 1, Hg(SeCN)Cl is precipitated in yellow needles, soluble in absolute alcohol. If the proportion is 3 : 1, $KHg(SeCN)_3$ crystallizes out as yellow needles, somewhat soluble in water, while if the proportion is 4 : 1, $K_2Hg(SeCN)_4$ is formed, easily soluble in water and alcohol, crystallizing from absolute alcohol in amber plates. Crystallin $CoHg(SeCN)_4$ and $ZnHg(SeCN)_4$ were formed by double decomposition from the potassium salt, showing the existence of the complex anion $Hg(SeCN)_4^{--}$, and thus indicating the relation of the selenocyanates to the thiocyanates. No complex salts containing cobalt (bivalent) or trivalent iron or chromium could be formed. From a solution of mercuric nitrate, sodium selenite precipitates the mercury salt, $HgSeO_3$, as a white crystallin powder, which is very soluble in a solution of sodium selenite, with formation of $Na_2Hg(SeO_3)_2$. Conductivity determinations showed unmistakable evidence of the existence of mercuriselenite anions, which are, however, largely hydrolyzed in dilute solution. $NaSeO_3.HgCl.2H_2O$ was also formed by the action of one molecule of $HgCl_2$ on one molecule of Na_2SeO_3.

The investigations of Flint on the complexity of tellurium have been continued.[3] Working on a kilogram of crude dioxide by fractionating the chloride by precipitation with water, the tenth fraction, which consisted of 23 grams, showed an atomic weight of 124.3, while the original material gave the accepted atomic weight of 127.5. Fractionating by solution in nitric acid gave the atomic weight of the less soluble portion as 126.51. Work with the less hydrolyzed portion in the first fractionation revealed some difference in properties from pure tellurium, and this portion is now being investigated. Tibbals[4] has prepared sodium telluride by fusing sodium and tellurium in a hydrogen atmosphere and recrystallizing from water with careful exclusion of air. Na_2Te crystallizes in colorless crystals which contain much water of crystallization. The solution dissolves metallic tellurium up to the composition Na_4Te_3. By double decomposition a number of metallic tellurides were prepared in the wet way for the first time, and the following are described: $ZnTe.H_2O$, $Ni_2Te_3.4H_2O$, which by heating goes into NiTe, $Co_2Te_3.4H_2O$, $Pb_2Te_3.4H_2O$, Ag_2Te, CuTe, Cu_2Te_3. A telluride of arsenic goes into solution in excess, indicating a telluro-arsenite. Gold and platinum are precipitated as metals from chloride solution, $TeCl_4$ being formed.

[1] *Z. physik. Chem.*, 70, II. *Arrhenius Festband*, 1.

[2] *Z. anorg. Chem.*, 63, 275.

[3] *Ibid.*, 68, 251.

[4] THIS JOURNAL, 31, 902.

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The influence of a second solute on crystallization is shown by work of Hauser and Herzfeld[1] on potassium dichromate. When to a hot, three-fourths saturated solution of the ordinary triclinic salt is added an equal quantity of a saturated solution of potassium thiocyanate, and the whole allowed to cool, the potassium dichromate crystallizes out in monoclinic prismatic plates of yellowish brown color with a bronze luster. The specific gravity of these crystals is 2.10, while that of the ordinary form is 2.67. These crystals are metastable and probably isomorphous with ammonium dichromate. By heating the carbonates with chromic acid in a closed tube, Briggs[2] has obtained cobalt chromate both anhydrous and as dihydrate, and also nickel chromate, $NiCrO_4$. The latter is stable in water and hardly attacked by nitric acid. By evaporating solutions of the carbonates with chromic acid in excess, Gröger[3] has prepared the dichromates of zinc, cadmium, copper and cobalt, all as hydrated salts. These dichromates have a great tendency to decompose into the normal chromate and higher chromates. By using the proper proportion of the constituents and evaporating in a vacuum over sulfuric acid, cadmium trichromate, $CdCr_3O_{10}.H_2O$, and copper tetrachromate, $CuCr_4O_{13}.2H_2O$, were obtained. The work of Weinland on hexa-acetato-trichromium bases has been continued.[4] Numerous salts of the tribasic cation $(Cr_3(CH_3.COO)_6(OH_2)_2)^{+++}$ are described, as well as of the cations $(Cr_3(CH_3.COO)_6(OH_2)(OH))^{++}$ and $(Cr_3(CH_3.COO)_6(OH_2)_2)^{+}$. Similar cations are formed with iron in the place of chromium, and also with Cr_2Fe and $CrFe_2$. Both chromium and iron cations have also been obtained with pyridine in the place of the water in the cation, and in the case of the chromium cation with NH_3 in the place of the water. Weinland calls attention to the fact[5] that in the official ferric acetate solution, the deep red color is due to the presence of the $(Fe_3(CH_3.COO)_3(OH)_2)^{+}$ cation. This base also lies at the foundation of the ordinary acetic acid reaction with ferric chloride. Bjerrum[6] has studied the conductivity and the transition velocity of the chlorochromisulfates, and has also prepared analogous sulfates in which the hexahydrated chromium atom of $(CrCl_2(OH_2)_4)(Cr(OH_2)_6)^{++++}$ is replaced by aluminium, by iron and by vanadium, and he has also prepared the corresponding bromosulfates.

In his investigations of molybdenum, Rosenheim[7] has prepared the so-called dichloride of Blomstrand and confirms the latter's trimolecular formula, Mo_3Cl_6. It crystallizes from hydrochloric acid with one molecule of acid and four of water. The loss of water and acid on heating show its constitution to be $(Mo_3Cl_6.H_2O)HCl.3H_2O$. With alkalies it gives $Mo_3Cl_4(OH)_2$ and with ammonia $(NH_4)Mo_3Cl_7(NH_3)$. The amount of its reduction of ammoniacal silver confirms the bivalence of the molybdenum. Rosenheim[8] has also further studied the double cyanides, which

[1] *Z. physik. Chem.*, 68, 175.
[2] *Z. anorg. Chem.*, 63, 325.
[3] *Ibid.*, 66, 7.
[4] *Ber.*, 42, 2997, 3881; 43, 2144. *Z. anorg. Chem.*, 67, 167, 250.
[5] *Arch. Pharm.*, 248, 337.
[6] *Z. anorg. Chem.*, 63, 140, 151.
[7] *Ibid.*, 66, 1.
[8] *Ibid.*, 65, 166.

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contain the $Mo(CN)_8$---- anion, and in which the oxidation with potassium permanganate and also with ammoniacal silver shows the molybdenum atom to be quinquivalent. The free acid $H_4Mo(CN)_8.6H_2O$ was prepared. The only suggestion regarding the valence is that the complex may be really $Mo_2(CN)_{10}''''''$, and the two molybdenum atoms united with each other; of this, however, there is no experimental evidence. Salts of the anion $MoO_2(CN)_4$---- were also prepared, the constitution being more probably $Mo(OH)_4(CN)_4$----. Ephraim[1] in his studies of the molybdates has prepared lithium, rubidium and cesium molybdates of numerous different ratios, as well as numerous phospho- and arseno-molybdates of these three alkalies, while Miolati[2] has prepared telluro-molybdates and formomolybdates, and Mazzucchelli,[3] oxalo-permolybdates.

A very full investigation of the methods for preparing metallic tungsten is described by Weiss.[4] Reduction by metallic aluminium from wolframite gives a regulus containing about 80 per cent. tungsten, and reduction of the amount of aluminium gave no better results, for while less iron and manganese were reduced, the same was true of the tungsten, as only 2/3 of the tungstic acid present was recovered as metal. This method can possibly serve to prepare a carbon-free alloy of tungsten with some iron and manganese for use in steel-making. Wolframite is completely resolved by fusion with sodium carbonate or caustic soda, and also with lime. In the last case, though its outward appearance seems unchanged, it is rendered largely soluble in hydrochloric acid. Fusion with calcium carbonate and salt is a method which may be of technical value. Tungstic acid can be reduced by zinc powder to a crystallin regulus containing at least 99.8 per cent. tungsten. No satisfactory method was found for the direct preparation of tungsten from scheelite, nor from the sulfide. By the use of a vacuum electric furnace tungsten can be satisfactorily fused, and the metal obtained is very resistant.

A number of uranium compounds have been studied by Wyroubow,[5] chiefly from a crystallographical standpoint. $U(SO_4)_2$ exists as octo- and nonohydrate, isomorphous with thorium sulfate. Four distinct types of uranyl oxalates of the alkalies were obtained.

Group VII.—A new form of apparatus for preparation of fluorine is described by Gallo,[6] and the result of experiments to prepare a compound of fluorine with oxygen. The mixed dry gases were passed through an ozone apparatus, and after a few moments a strong explosion occurred, shattering the apparatus. Gallo thinks it probable that there had been formed an exceedingly unstable endothermic compound of oxygen and fluorine. A series of double fluorides of thallium has been prepared by Ephraim,[7] including those of manganese, antimony, vanadium, tantalum, and tungsten.

The work of Richards on atomic compressibility has been continued,[8]

[1] *Z. anorg. Chem.*, 64, 258, 263; 65, 233, 237.
[2] *Z. physik. Chem.*, 70, II. *Arrhenius Festband*, 330.
[3] *Atti accad. Lincei, Rome*, [5] 18, ii, 259.
[4] *Z. anorg. Chem.*, 65, 279.
[5] *Bull. soc. franç. min.*, 32, 340.
[6] *Atti accad. Lincei, Rome*, [5] 19, i, 206, 295, 753.
[7] *Ber.*, 42, 4456.
[8] *Z. physik. Chem.*, 71, 152.

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comparing the compressibility of the halides of potassium, sodium, thallium and silver, with that of the constituent elements. While the molecular compressibility is in every case less than that of the constituents, there is a marked difference in the amount of this lessening. For example, thallium is hardly one-tenth as compressible as sodium, yet its halides are more compressible than those of sodium. The facts indicate that the specific volume of compounds is strikingly dependent upon the chemical affinities of the constituents.

Bourion[1] has further developed his work on the preparation of anhydrous chlorides by heating the oxide in a current of chlorine saturated with chloride of sulfur. The chlorides of the rare earths are readily formed by this method and a large number of them are described, as well as methods of determining tungsten and the quantitative separation of cerium, thorium and glucinum. In his work on double halides, Ephraim[2] finds that manganese has little tendency to form double bromides, $CaMnBr_4.4H_2O$ being the only one he could prepare. Two calcium-zinc chlorides were found, $CaZnCl_4.5.5H_2O$ and $Ca_2ZnCl_6.6H_2O$, but only one of each of the other alkaline earths, $SrZnCl_4.4H_2O$ and $BaZnCl_4.2.5H_2O$. The sodium and ammonium zinc iodides are constituted after the type $NaZnI_3$, while the potassium salt is K_2ZnI_4, and the double iodides of the alkaline earths are of the same type. All the double iodides are hydrated. A number of chlorates and perchlorates of ammonia bases are described by Salvadori,[3] who suggests a strongly ammoniacal solution of ammonium perchlorate for the separation of cadmium from copper. $Cd(NH_3)_4(ClO_4)_2$ is insoluble and immediately precipitated, while the copper salt is precipitated only slowly, even from concentrated solutions. A weakness of the separation consists in the fact that the cadmium precipitate carries copper, if present, down with it, though the method serves excellently to detect cadmium in the presence of copper. The resistance of chlorates, perchlorates, iodates, periodates and bromates to reduction is discussed by Vitali,[4] and he finds that chlorates are reduced by aluminium in dilute sulfuric acid while perchlorates are not. No distinction was found between iodates and periodates, and both these and bromates resemble chlorates in showing less resistance to reducing agents than the perchlorates. The so-called hypoiodic acid is considered by Skrabal and Buchta[5] to be really a base, I.OH, which is relatively stable in very dilute solutions. In the presence of hydrochloric acid ICl is formed, which by great HCl concentration is exceedingly stable. In sulfuric acid solution the base is unstable owing to hydrolysis, but its stability is much increased by the presence of free halogens, in which case ICl_2OH and I_3OH are formed. Free iodine hydroxide decomposes, according to the acidity of the solution, into iodine and iodic acid.

Group VIII.—The relation of iron solutions to nitric oxide has been studied by Manchot,[6] who finds the absorption of NO is less in ferrous sulfate solutions containing dilute sulfuric acid than in those of pure

[1] *Ann. chim. phys.*, [8] 20, 547.
[2] *Z. anorg. Chem.*, 67, 376, 379.
[3] *Gazz. chim. ital.*, 40, ii, 9, 19.
[4] *Giorn. farm. chim.*, 59, 18.
[5] *Chem.-Ztg.*, 33, 1184.
[6] *Ann.*, 372, 153, 179.

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water, but that in solutions containing concentrated sulfuric acid (82 per cent.) a maximum of one molecule of NO to one molecule of $FeSO_4$ is reached. The same limit is attained in a 34 per cent. HCl solution. Many other solvents and additions to the solutions were tested, but in no case was the maximum of 1 : 1 passed. On the other hand, while nitric oxide is not absorbed by aqueous solutions of ferric sulfate, in the presence of concentrated sulfuric acid (90.6–97.6 per cent.) a maximum absorption of two molecules NO to each iron atom was attained, and the compound formed may be considered as $Fe_2(SO_4)_3.4NO$. From this it seems to follow that since in hemoglobin the absorption of nitric oxide is in the proportion of two molecules for each atom of iron, the iron of the blood is in the ferric condition. The compound $2FeSO_4.NO.13H_2O$ was isolated, which Manchot considers to be $FeSO_4.NO$ crystallized with $FeSO_4$. Le Chatelier[1] and also Konstantinov[2] have investigated the phosphides of iron, the latter with especial reference to the metallurgy of the metal, a diagram of the iron-phosphorus system being given. Out of the nine different phosphides which have been described by different workers, Le Chatelier finds the following only to be chemical individuals: Fe_3P, Fe_2P, FeP and Fe_2P_3. The preparation and properties of each are described.

Ephraim[3] shows that the NH_3 of $CoC_2O_4.4NH_3$ is progressively replaced by H_2O by standing in the air, $CoC_2O_4.4H_2O$ being ultimately formed. The latter salt can be directly prepared from aqueous solution. Each member of the series was isolated. Of the double cobalt oxalates both $(NH_4)_2CoOx_2.6H_2O$ and $(NH_4)_4CoOx_3.6H_2O$ were prepared. Three of the nitrite groups in sodium cobaltinitrite (sodium nitritocobaltiate) can be replaced according to Hofmann and Buchner[4] by the hydroxyl group by the action of guanidine carbonate, guanidine or sodium-guanidine salts of the trihydroxy-trinitrito-cobaltiate, $Co(NO_2)_3(OH)_3^{---}$, being formed. From certain differences between the guanidine and the sodium-guanidine salts, it is conjectured that the anion may exist in two isomeric forms.

In preparing osmium for atomic weight determination, Gutbier and Maisch[5] put it into solution by repeated heating with salt in chlorine, and from the sodium hexachloro-osmate, which could not be obtained in a pure condition, prepared the other alkali chlorides by double decomposition. The chloro-osmates decompose slowly on standing in aqueous solution. The rubidium and cesium salts are almost insoluble in water. Ruff[6] has also studied the chlorides as well as the oxides of osmium. To prepare osmium tetroxide he distils with concentrated sulfuric acid and chromic acid, instead of nitric acid. Reduction in acid solution with alcohol, formaldehyde, or hydrazine gives the dioxide, but in a colloidal condition which is difficult to filter. It may be precipitated by barium sulfate. It is better, however, to precipitate with alcoholic potash, heat on a water bath, and exactly neutralize with sulfuric acid. The

[1] *Compt. rend.*, 149, 709.
[2] *J. Russ. Phys. Chem., Soc.* 41, 1220.
[3] *Ber.*, 42, 1624.
[4] *Ibid.*, 3389.
[5] *Ibid.*, 4239.
[6] *Z. anorg. Chem.*, 65, 429.

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dioxide is then precipitated completely and settles well. If filtered at once it decomposes explosively when dried at 100°–150°, but if heated for several hours on the water bath before filtering, it may be gradually heated in a carbon dioxide atmosphere to 250° and weighed. The use of titration with potassium permanganate for the estimation of osmium is possible with certain precautions, but presents few advantages. When osmium is heated in chlorine, the product obtained depends upon the temperature and the rapidity of cooling. If rapidly cooled, the chief product is $OsCl_3$, which heated in a vacuum to 560°–600° decomposes into the volatil $OsCl_4$ and leaves the non-volatil $OsCl_2$. By slow cooling $OsCl_4$ is obtained. It is insoluble in water and other solvents except the strong oxidizing acids. $OsCl_2$ is also but slightly soluble. On the other hand, $OsCl_3$, even in anhydrous condition, is soluble in water, unlike the anhydrous trichlorides of the other platinum metals.

A large number of hexachloro-iridates and hexabromo-iridates of organic bases have been prepared by Gutbier.[1] Iridium tetrachloride was made by passing chlorine over iridium mixed with KCl or NaCl, at a low red heat, from this preparing the ammonium salt by precipitation with NH_4Cl, decomposing the ammonium in this by chlorine, and finally distilling the water and HCl off at 40° in a moderate vacuum. The organic salts were formed by precipitating hexachloro-iridic acid with solutions of the chlorides of the bases. When bromides of the bases were used, the precipitated salts were still *chloro*-iridates, but on boiling these with hydrobromic acid, they were changed over into the hexabromo-iridates. Bromine does not act directly on iridium, nor on a mixture of iridium with sodium bromide to more than a very slight extent, but the chloride is converted into the bromide by boiling with excess of hydrobromic acid. In general the bromo-salts are more soluble than the corresponding chloro-salts. Vèzes and Dufour[2] have made an extended study of the complex derivatives of iridium containing oxalic cid. By heating chloro-iridates or iridites with potassium oxalate, derivatives of dichloro-dioxalato-iridous acid are formed, several of which are described. The free acid, $H_3IrCl_2(C_2O_4)_2.4H_2O$, was also obtained. By boiling the salts of this acid with a concentrated solution of a nitrite, one-half the oxalate group is exchanged for nitrite groups, and a series of dichloro-dinitrito-oxalato-iridites was obtained. Work on iridium sulfates has been continued by Delépine,[3] who finds two series of salts, one derived from $(Ir(SO_4)_2(OH)_2)^{---}$, and the other from $(Ir(SO_4)_2(OH_2)OH)^{--}$. The change from one anion into the other seems to present a case of inorganic tautomerism. Delépine has also prepared silver chloro-iridate, which is unstable and goes over on standing into the iridite, and also the ammonia-silver iridite, $Ag_3(NH_3)_6.IrCl_6$, which was supposed by Claus to be merely another form of silver chloro-iridite. Thallium chloro-iridite and chloro-iridate were also prepared.

Compounds of platinum with a valence of three and with a valence of six have been discovered by Wöhler and Martin.[4] By anodic oxidation of a solution of hydrated platinum dioxide in caustic potash at low tem-

[1] *Z. physiks. Chem.*, 69, 304. *Ber.*, 42, 3905, 4770.
[2] *Bull. soc. chim.*, [4] 5, 869, 872; 7, 507, 512.
[3] *Compt. rend.*, 149, 785, 1072. *Bull. soc. chim.*, [4] 5, 1084.
[4] *Z. Elektrochem.*, 15, 769, 791. *Ber.*, 42, 3326, 3958, 4100.

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perature, thin gold-like scales are obtained which are probably $K_2O.3PtO_3$. The potassium is removed by dilute acid and the trioxide, PtO_3, is obtained, which is extremely unstable. By the careful chlorination of $PtCl_2$, or dechlorination of $PtCl_4$ at 390°, $PtCl_3$ was obtained as a greenish black powder, which is slightly soluble in cold water, and which dissolves rapidly in boiling water with the formation of the acid H_2PtCl_3O, some hydrolysis also taking place. By precipitation with sodium carbonate pure platinum sesquioxide hydrate was obtained, but the sesquioxide could not be prepared. The hydrate dissolves in hydrochloric acid but the solution immediately decomposes into a mixture of chloroplatinous and chloroplatinic acids. If, on the other hand, cesium chloroplatinite in dilute solution is treated with chlorine water a dark green precipitate of the "sesquichloride," or pentachloride, Cs_2PtCl_5, is obtained, which has a strong tendency to decompose into the chloroplatinite and chloroplatinate. According to Werner's nomenclature, the platinum acids would receive the following names: H_2PtCl_4, tetrachloro-plat*o*-acid; H_2PtCl_5, pentachloro-plat*i*-acid; H_2PtCl_6, hexachloro-plat*e*-acid; H_2PtO_4, plat*o*n-acid. In addition to the iridium salts spoken of above, Gutbier[1] has prepared similarly a large number of salts of bromoplatinic acid with organic bases. His bromoplatinic acid was prepared by evaporating chloroplatinic acid several times on the water bath with hydrobromic acid, the last time with the addition of bromine. The free acid, $H_2PtBr_6.9H_2O$, was obtained by evaporation over lime. The two isomers of the compounds of platinum dichloride with organic sulfides are accounted for by Werner by stereoisomerism. The third modification of the methyl sulfide salt, it has been suggested, may be constituted after the type of the green salt of Magnus. This, Chugaev and Subbotin[2] now show to be the case, its constitution being, in fact, $(Pt.4(CH_3)_2S)PtCl_4$. Further, it is found that other organic sulfides can form platinum salts after this same type. By the action of formaldehyde on a solution of potassium chloroplatinate and selenium dioxide in an excess of caustic potash, Minozzi[3] has obtained platinum triselenide, $PtSe_3$, which on heating to a low red heat in carbon dioxide gives the diselenide, $PtSe_2$. Both are stable compounds, little acted on by acids.

The experiments of Fischer and Schröter on argon have been extended[4] and 45 metals examined in the electric arc in liquid argon. In no case could argon compounds be obtained, nor was there any evidence of the formation of any such even transitionally.

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NOTES.

The Efficiency of the Borax Bead Tests for Nickel and Cobalt.—In order to determine the reliability of the borax bead tests for nickel and cobalt (in the presence of each other), a few simple tests were carried out. As the object of these experiments was to ascertain the efficiency

[1] *Ber.*, 42, 4243.
[2] *Ibid.*, 43, 1200.
[3] *Atti accad. Lincei, Rome*, [5] 18, ii, 150.
[4] *Ber.*, 43, 1435, 1442, 1454, 1465.

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of these bead tests as applied in qualitative analysis, only that degree of refinement of method was practiced which obtains in careful qualitative analysis.

Solutions of nickel and cobalt nitrates were mixed in varying proportions and the point determined at which either of the metals interfered with the other. The two metals were completely precipitated as sulfides by hydrogen sulfide, in the presence of a sufficient excess of ammonia. Portions of the freshly precipitated sulfides were then fused in the borax beads and the beads, which were of approximately uniform size, were viewed by daylight. All tests were made in duplicate and all the beads were fused in both the oxidizing and reducing flames.

The following results were obtained:

Parts nickel.	Parts cobalt.	Results when held in oxidizing flame.	Results when held in reducing flame.
1	1	Blue bead	Blue bead
2	1	Blue bead	Blue bead
3	1	Blue bead	Blue bead
5	1	Blue bead	Blue bead
7	1	Blue bead	Blue bead
10	1	Blue bead	Blue bead
20	1	Blue bead	Blue bead
30	1	Blue bead	Uncertain violet
40	1	Uncertain brownish	Uncertain brownish
45	1	Uncertain brownish	Uncertain brownish
50	1	Brown bead	Brown bead

The same results as above were also obtained from the hydroxides precipitated from similar solutions by sodium hydroxide.

An examination of the above results indicates that:

One part of cobalt can be detected in the presence of thirty of nickel. If, however, the ratio of the nickel to cobalt be increased, uncertain results are obtained until the ratio is about fifty to one when a decidedly brown bead shows the presence of nickel. Again one part of cobalt in fifty of nickel would certainly be lost if the bead tests were solely relied upon. It is evident, therefore, that the borax bead tests for nickel and cobalt can serve only as confirmatory tests, and that reliance can be placed upon them only when the results are affirmative.

L. J. CURTMAN.
P. ROTHBERG.

COLLEGE OF THE CITY OF NEW YORK,
November, 1910.

A Good Substitute for the Platinum Triangle.—While working with an alloy of nickel and chromium in form of a resistance wire manufactured by the Driver-Harris Wire Co., its resistance to the common laboratory fumes and oxidation at the temperature which it is possible to obtain with the ordinary blast lamp, made it occur to the writer that this wire might be used to advantage to replace the ordinary platinum triangle.

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In order that the use of this alloy might be experimented with for this purpose, several triangles were made. This was accomplished, in each case, by twisting together the ends of three pieces of No. 13 nichrome wire, each about four inches long. The triangles made in this manner were used to support platinum crucibles, which were ignited side by side with others supported either on platinum or common pipe-stem triangles. The crucibles showed about the same loss in weight when ignited by similar means on any of the triangles mentioned. This was true whether they were ignited over a Bunsen burner, blast lamp, using city gas (containing a large amount of sulfur) or a gasoline blast lamp. The nichrome triangles, themselves, when used with city gas, either over the Bunsen or the blast, lost, at most, one milligram an hour and at times showed either a slight gain or no loss at all. When the gasoline blast was used (this gas did not contain any sulfur) the loss of either the crucibles or the triangles was not more than two- or three-tenths of a milligram an hour. One of these triangles will outlast a number of pipe-stem triangles and at the same time allow a higher temperature to be obtained in the crucibles. In fact they make a good substitute for platinum triangles and can be made for the price of a pipe-stem triangle. This article has been put on the market by H. C. Stoelting & Co., Chicago.

R. C. BENNER.
UNIVERSITY OF ARIZONA,
TUCSON.

ON THE ACTION OF CHROMYL CHLORIDE ON INDIA RUBBER.

[PRELIMINARY COMMUNICATION.]

BY D. SPENCE AND J. C. GALLETLY.

Received November 23, 1910.

The singular reactivity of india rubber towards sulfur chloride is well known, for on the results of this activity depends the technical process of "cold vulcanization." As far as we know however the action of chromyl chloride on rubber has never been investigated, a fact the more surprising in view of the work of Etard,[1] of Bredt and Jagelki[2] and of Henderson[3] and his scholars on the action of chromyl chloride on the terpenes, and of the close relationship which was at one time supposed to exist between india rubber and the terpene hydrocarbons.

In these, our preliminary researches, we have endeavored to investigate the action of chromyl chloride on rubbers of different botanical origin. We have actually found that in every case this substance reacts with india rubber to form a perfectly definit compound of the formula $C_{10}H_{16}.2(CrO_2Cl_2)$ analogous to the compound formed by the action of

[1] *Ann. chim. phy .*, 22, 218 (1881). *Compt. rendus*, 116, 434 (1893).

[2] *Ann.*, 310, 112 (1899).

[3] Henderson, *J. Chem. Soc.*, 55, 45 (1889). Henderson, Gray, Smith, *Ibid.*, 83, 1299 (1903). Henderson, *Ibid.*, 91, 1871 (1907). Henderson and Heilborn, *Ibid.*, 93, 288 (1908).

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chromyl chloride on the terpenes. This compound is insoluble in any of the usual organic solvents but dissolves readily in water, by which it is decomposed.

We have found that the behavior of chromyl chloride towards india rubber is not exactly similar to its action on the terpenes. In the first instance the addition of chromyl chloride to rubber is not accompanied by the same evolution of heat.[1] Even in a concentrated solution of india rubber in carbon disulfide only a mild evolution of heat occurs on the addition of chromyl chloride.

In the second place, the decomposition of the chromyl chloride derivative of rubber by water is not so complete as it is in the case of the analogous compounds of the terpenes. The chromyl chloride derivative of india rubber dissolves freely and completely in water giving a perfectly clear but dark green solution and from this solution only on heating a brown gummy flocculent mass separates. None of the decomposition products appear to be volatil in steam as they are in the case of the terpenes.

By decomposing the chromyl chloride derivative of india rubber by water and extracting the aqueous solution with ether, we have isolated in an impure state a substance with aldehyde reactions, giving a derivative with phenyl hydrazine. From the same aqueous solution we have separated an insoluble substance containing chromium and chlorine in apparently perfectly definit amounts. This latter substance is insoluble in all organic reagents and is still of complex colloidal character.

By dialyzing the aqueous solution of the chromyl chloride derivative of rubber into water the chromium and chlorine can be almost entirely removed. An opalescent, colloidal solution is obtained in this way, which remains unchanged even on boiling. From this solution, however, we have separated the two substances mentioned above, admixed with a very uninviting-looking mass of resin-like decomposition products.

From the still colloidal character of the decomposition products of the action of water on the chromyl chloride compound, it is evident that just as the action of chromyl chloride on rubber is not so vigorous, in the first instance, as the action of this reagent on the terpenes, so also the decomposition of the chromyl chloride compound of india rubber is not so complete as in the case of the corresponding compounds of the terpenes. On account of the interesting character of the products of this reaction, and of the mild oxidative nature of the same we are engaged in investigating still further the nature of the changes resulting from the oxidation of rubber by chromyl chloride. We believe that the Etard reaction will serve as a means of throwing further light on the constitution of the rubber hydrocarbon.

[1] See Henderson, *J. Chem. Soc.*, 91, 1871 (1907).

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Experimental.

Preparation of the Chromyl Compound.—The chromyl chloride used in our experiments was freed from chlorine as far as possible by repeated distillation under diminished pressure in an atmosphere of carbon dioxide. To a 2.25 per cent. solution of rubber in dry carbon disulfide, equivalent to 1 molecule of rubber, a quantity of chromyl chloride, representing slightly more than 2 mols. CrO_2Cl_2, in carbon disulfide (5 per cent. solution) was slowly added in small quantities at a time with vigorous agitation.[1]

The addition of chromyl chloride to rubber goes so smoothly in this way that it is unnecessary to cool the reacting solutions with ice as in the case of the terpenes.

The voluminous dark brown precipitate which quickly separates from the carbon disulfide is washed by decantation till free from chromyl chloride, drained as rapidly as possible at the pump and dried *in vacuo*.

0.202 g. substance; 0.0694 g. Cr_2O_3

$C_{10}H_{16}.2(CrO_2Cl_2)$ Calculated Cr = 23.31%

Found Cr = 23.51%

The chromium content of the product from the action of chromyl chloride on rubbers of various botanical origin was found to be as follows:

Name of rubber.	Weight of chromyl chloride compound. Gram.	Weight Cr_2O_3. Gram.	Cr found. $C_{10}H_{16}.2(CrO_2Cl_2)$ = 23 31 Cr.
Extra Fine Para	0.296	0.1022	23.63
Island Medium Para	0.3798	0.131	23.61
Ficus elastica	0.3584	0.1224	23.35
Maniçoba	0.424	0.143	23.09
Landolphia owariensis	0.4154	0.1382	22.77

The product of the reaction is a dark brown powder insoluble in organic solvents, but readily soluble in water, by which it is immediately decomposed. It absorbs moisture on exposure to air, decomposing rapidly.[2]

Decomposition of the Chromyl Chloride Derivative of Rubber by Water.—Nine grams of the chromyl chloride compound of india rubber gave a clear but dark green solution when slowly added to 200 cc. water. Steam distillation of this solution failed, however, to give volatil products. From the solution on standing and more rapidly on boiling, a brown gummy mass separated and from this by extraction with ether or, better still, by chloroform, a resin-like substance was isolated.

[1] Experiments conducted using 4 mols CrO_2Cl_2 to 1 mol of rubber gave a compound containing only two mols of added CrO_2Cl_2. The removal of the resins and proteins from the rubber prior to treatment with CrO_2Cl_2 does not appear to be necessary.

[2] On account of the ease with which this compouud decomposes in moist air our experiments to utilize the reaction between rubber and chromyl chloride as a method for the quantitative estimation of rubber were fruitless.

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The resinous extract dissolved readily in alcohol but so far attempts to obtain crystallization have failed. The extract reduced Fehling solution, reacted with decolorized fuchsin solution, decolorized dilute potassium permanganate acidified with dilute sulfuric acid, dissolved readily in 1 per cent. sodium hydroxide solution giving an intense yellow coloration on heating. From this extract by treatment with phenylhydrazine, we have isolated in an impure state a small quantity of a crystallin compound, melting at 92° (unsharp).

The decomposition of the chromyl chloride compound of rubber by water would appear, therefore, to yield as one product an aldehyde. The brown amorphous substance left after extracting the gummy precipitate formed on boiling the aqueous solution of the chromyl compound was apparently of complex colloidal character. When boiled with alcohol till free from the last traces of the resinous by-product it is a brown powder, insoluble in all organic solvents and in dilute acid. It dissolves slowly in dilute alkali and contains chromium and chlorine in apparently definit amounts.

Decomposition by Dialysis.—Ten grams of the chromyl compound were dissolved in 200 cc. of water and the solution thus obtained was dialyzed for 48 hours in a gentle stream of water and for a further 24 hours in a stream of distilled water. A small quantity of hydrated oxide separated inside the dialysis tube but this was readily removed by filtration. The pale yellow, but somewhat opalescent, colloidal solution left after dialysis is perfectly stable even above the ordinary temperature. It was readily decomposed, however, by warming with a trace of acid. Even by passing a slow current of carbon dioxide through the solution warmed on the water-bath decomposition takes place and a light brown, gummy mass separates which consists of a mixture of the alcohol-soluble resinous products extracted by chloroform with the insoluble substance isolated directly from the aqueous solution of the chromyl compound. Some analyses for Cr and Cl of the insoluble product isolated by different means and purified as far as possible are here recorded:

	Cr Per cent.	Cl Per cent.
(*a*) Separated from aqueous solution after extracting with chloroform	4.64	....
(*b*) Aqueous solution decomposed by boiling, insoluble product separated and extracted by alcohol	4.62	4.48
(*c*) By dialysis and alcohol extraction	4.81	....
	4.44	....
(*d*) Ditto	4.40	4.22

It is useless at the present stage of our investigation to offer any explanation for the singular nature of the changes resulting from the decomposition of the chromyl chloride compound of india rubber by water.

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We are now engaged in isolating the aldehyde and the insoluble chromium compound in quantities sufficient to enable us to investigate them still further.

RESEARCH LABORATORIES,
THE DIAMOND RUBBER CO.,
AKRON, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE RED AND WHITE SILVER SALTS OF 2,4,6-TRIBROMOPHENOL.[1]

BY HENRY A. TORREY AND W. H. HUNTER.

Received December 16, 1910.

Only one silver salt of 2,4,6-tribromophenol was mentioned in the chemical literature at the time we took up this research. This was prepared by Purgotti[2] from the calcium salt, and described as an orange-red precipitate. In preparing this salt by precipitation of a solution of the sodium salt with silver nitrate in excess, we happened to leave a partly washed red precipitate standing on the filter for some hours; when we came to finish the washing, we found it had become completely decolorized, with the exception of some particles which had dried on the edge of the filter. A determination of silver in the air-dried white salt indicated that it was isomeric with the red salt, which was amply confirmed by later analyses of pure specimens.

A study of the conditions under which the white isomer was formed showed that it could be obtained from the red compound by carrying on the precipitation from very dilute solutions, or from a boiling solution, or by solution of the red salt in a little ammonia, and precipitating the white salt from this solution by the addition of more silver nitrate solution. Of these methods, the last is the only one which gives us a pure white salt, and can be used to advantage as a method of preparation. It also furnishes us with a probable explanation of the formation of the white salt from the red when exposed to the air of the laboratory, which may well have contained ammonia.

At this point of our work, a preliminary paper was published,[3] and this called forth immediately a paper[4] from Hantzsch's laboratory, in

[1] This research was suggested by the late Professor Henry A. Torrey and the experimental work was done under his direction but the explanation of the observations and the writing of the paper were deprived of the benefit of his supervision by his too early death. C. L. JACKSON.

The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by William Hammett Hunter.

[2] *Gazz. chim. ital.*, 16, 527 (1886).

[3] *Ber.*, 40, 4332 (1907).

[4] *Ibid.*, 40, 4875 (1907).

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which he confirmed our results, added another case of the kind which he had discovered, and courteously left the field to us.

In continuing the work, a method of preparing the white salt without previous formation of the red one was worked out, based on the change produced by ammonia, which was more economical of time and silver nitrate. It consisted in adding to the solution of the sodium salt of tribromophenol a few drops of ammonia, which prevented the formation of the red salt, but allowed the precipitation of the white on the addition of rather more silver nitrate than would be required to precipitate the red salt in a solution free from ammonia. This method also helps to prove that the white salt is the stable, and the red salt the labil form.

Since the appearance of the paper of Furcht and Lieben,[1] who describe a white and yellow levulinate of silver, but ascribe the color of the yellow salt to an impurity, it is worth while to point out the reasons for believing that the red color of the silver tribromophenolate is not due to an impurity. Our analyses of both salts agree with the theoretical percentages. The white salt is made from the red without the appearance of any colored by-products. Moreover, some white salt was converted into tribromophenol, and from this sample the red salt was obtained just as easily as from a sample of the phenol freshly prepared.

Nor are the salts of tribromophenol the only case of the kind known. In the paper mentioned, Hantzsch describes two forms, a white and an orange, of the silver salt of dibromoparacresol, in addition to corroborating our work on the salts of tribromophenol. He investigated a number of other phenols, finding white salts in some cases, colored salts in others, but in no other case did he find both forms.

On our part, we have been able to find two other cases in which a red precipitate occurs first, rapidly becoming spontaneously converted into a white form, but we could only isolate the white forms for analysis, as the velocity of transformation of the red salts was too great to permit of their isolation. In view of the purity of the materials used, and of the white salt isolated in each case, there can be no doubt that the red salts formed were strictly analogous to those of tribromophenol and dibromoparacresol. An additional piece of evidence is that ammonia hastens the change in exactly the same manner as that of the tribromophenol salts.

These two cases were the silver salts of 2,4,6-tribromoresorcinol monomethyl ether, and of 3,4,6-tribromoguaiacol.[2]

[1] *Bull. soc. chim.*, [4] 5, 1069 (1909).

[2] The position of the bromine in this substance has never been determined beyond question, but as it is formed from the 4,6-dibromoguaiacol there seems little doubt that the third atom of bromine has taken the 3, rather than the 5 position, which stands between the two atoms of bromine already present. It may be added that the position of this third atom of bromine seems in no way important in our work.

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The silver salt of tetrabromoguaiacol behaves in the same way, except for the fact that at the very instant of precipitation, the silver salt seems to be white. This appearance is evanescent, however, the red salt appearing immediately, and changing rapidly in its turn to a permanent white. This salt was not analyzed, as it seemed useless to analyze any more white salts.

We next tried precipitation in acetone instead of water, in the hope of isolating the red salts of the two phenols whose white salts had been analyzed. We were not able to get an acetone solution of the potassium salt of tribromoresorcinol monomethyl ether, but we obtained a noteworthy compound from tribromoguaiacol, a yellow potassium derivative, giving a yellow solution in acetone. Further, this yellow solution gave a red precipitate with an acetone solution of silver nitrate which, however, blackened from decomposition before it could be isolated. No formation of a white silver salt was observed, possibly because the red compound decomposed before this change began. This yellow potassium derivative seems as if it might be nearly related to the red silver salt. Analyses for bromine and potassium pointed toward its having the composition of a potassium salt with one molecule of crystal water, or of an addition product of tribromoguaiacol and potassium hydroxide. It was prepared by the action of solid caustic potash on an acetone solution of tribromoguaiacol and was a yellow solid giving a yellow solution in pure dry acetone, which was immediately decolorized by the addition of a little water. The dry yellow substance also dissolved slowly in water, giving a colorless solution. It is intended to investigate this interesting compound in the near future.

We were unable to obtain any difference in chemical behavior between the two salts, acids, alkalies, alkyl iodides, and other compounds with more or less reactive halogen atoms all acting in the same way with each isomer. Hantzsch, indeed, found a difference of a degree or two in the melting points of the ethers obtained from the two salts, but it is our opinion that it was accidental, as suggested by him. Experimental work along this line was abandoned only when there seemed no obvious point of attack left untried. Kruyt[1] has recorded his inability to solve this problem along physico-chemical lines.

In the course of the work with alkyl halides, we found that alkyl iodides, if used without a solvent, gave with the silver salts of tribromophenol a very strange series of reactions consisting in the appearance of a green color in the solid salt, accompanied by a blue color in the alkyl iodide, which in a few minutes became light yellowish brown, the solid in the meantime having taken on the appearance of silver iodide. The product of the reaction found in solution in the alkyl iodide, and making up part

[1] *Ber.*, 43, 543 (1910).

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of the precipitate, was a white organic compound, containing neither silver nor an alkyl group, and on analysis yielding about 64 per cent. of bromine, but no iodine. The same product was obtained with methyl, ethyl, or allyl iodide. Only enough work was done on it to show that there was no difference in the behavior of the two silver salts, but it is proposed to study it in much further detail at a later date.

Any explanation of the two salts must show that they can behave in the same manner toward reagents; for instance both give tribromophenol with acids, normal ethers with diluted alkyl iodides, and even the same abnormal reaction with the undiluted iodides.

Our present knowledge of the facts may be summed up as follows: in the case of five phenols, we have a colorless compound giving two silver salts, one red and one white, and these two salts have not been shown to act differently toward any reagents.

In determining the type of isomerism represented by these salts, the fact of their forming identical reaction products precludes the idea that they are chemical isomers, and leaves as the only probable explanations physical isomerism, polymerism, or tautomerism.

The question next arises, are they physical isomers? The hypothesis that they are simply two different solid modifications of the same compound accounts for all the chemical relationships, even to the change of the red salt into the white by ammonia solutions, but there are two valid objections to it. First, it should be possible to go from the white salt to the red, and if this is possible, the conditions for doing it have not yet been found. Second, and more important, not a case could be found in the literature, in which such a change is accompanied by a change in color. Obviously, phase changes accompanied by a change in water of crystallization do not come into this class.

Polymerism, on the other hand, is considered by Hantzsch to be a plausible explanation of the case. But Hantzsch himself has pointed out that the colorless derivative in cases of chromoisomerism may be safely presumed to have the normal formula, and it has been observed that in cases of polymerism, the monomolecular form appears first, and is less stable than its polymer, while if our salts are polymeric, the reverse is the case, the red salt appearing first, and being less stable than the white.

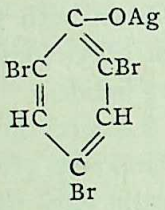
Again, this explanation would seem to require such a great difference in chemical activity as to preclude the likelihood of a duplication of the chemical action in the two cases. Especially is this probable in the case of the abnormal reaction with alkyl iodides discovered by us, which is so different from the normal behavior of silver salts as to lead to the conclusion that two molecules which give it must be far more like than polymers usually are. Nor can a supposed conversion of one form into

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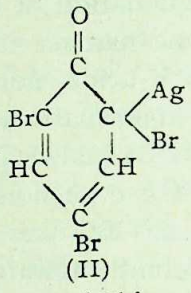
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the other during the reaction be used to avoid this difficulty, as it can hardly be supposed that cold methyl iodide could turn a polymer into the monomolecular form, or *vice versa*.

If these objections to the other theories are of sufficient weight, tautomerism is left as the sole explanation of the phenomenon, and if we ascribe the normal formula I to the white silver salt of tribromophenol, the



(I)



(II)

best formula for the red salt is II. The para form of this arrangement is also possible, but seems less probable, since the red color resembles the ortho rather than the para quinones, and all the five phenols which show this peculiarity have a bromine atom ortho to the hydroxyl, while Hantzsch's dibromoparacresol does not possess a para bromine atom. This is, however, a matter of slight importance, as the same arguments apply to both forms.

The chief objection to this formula was raised by Hantzsch after the formula was proposed tentatively in our preliminary paper: it contains silver tied directly to carbon, and to the same carbon atom as bromine. If silver could behave thus, he pointed out that mercury would have an even greater tendency to attach itself in a similar way, and therefore, should give colored salts, and yet the mercury salts of tribromophenol and other phenols studied by Hantzsch and Auld[1] were white. The analogy is not complete, however, for the salts mentioned were mercuric salts, which resemble silver salts only remotely. A much better experiment for the case in hand would be to take the mercurous salts of phenols, as mercurous mercury is very like silver, and we have still the great tendency which mercury shows to unite to carbon. This experiment was tried by us, and yellow salts were obtained from trobromophenol and tribromoresorcinol, and an orange salt from triiodophenol. It was proved further by analysis that these colors were not due to the presence of basic salts. Moreover, yellow precipitates were obtained under like conditions with tetrabromoguaiacol and with tribromoresorcinol monomethyl ethers, though these were not analyzed. Hantzsch's argument, therefore, from the analogy between our red salts and the corresponding mercury salts, is converted from an objection into a confirmation of formula II, since colored mercurous salts were obtained from phenols which gave red silver salts.

[1] *Ber.*, 39, 1105 (1906).

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Another objection to this formula is that it would seem as if it could not give the same reaction products as the normal salt; for instance, different ethers would be expected from the two salts, whereas both salts give the same ether and the same abnormal reaction with alkyl iodides. It must be remembered, however, that in the case of compounds having the quinoid-benzenoid isomerism indicated by our formulas, it is the rule rather than the exception that they give identical chemical reactions. The difficulty is rather to find reactions which will prove a difference between the two isomers, and usually the simple fact of one form being colorless, the other colored, has been taken as sufficient for ascribing such an isomerism as the cause of the difference in color.

It is fully recognized that arguments such as the above do not and can not prove the correctness of the explanation given for the structures of the two salts, but it would seem that it can be claimed with safety that the formula proposed for the red salt is open to less serious objections than any of the other explanations of the phenomena which we have considered.[1]

Experimental Part.

The tribromophenol was recrystallized from dilute alcohol till it showed the constant melting point 92°, which is that given by Post,[2] who also could not reach the higher temperature given by Körner[3] and Sintenis.[4]

The ordinary method used for making sodium salts of phenols in this work was to dissolve the phenol in a slight excess of alkali containing only a trace of chloride, and add very dilute acetic acid until a slight permanent precipitate was formed, when the mixture was shaken to coagulate the fine precipitate, and filtered. The solution of the tribromophenol sodium salt made in this way was always alkaline to phenolphthalein.

Red Silver Salt of Tribromophenol.—This salt, which was discovered by Purgotti, was made by adding a dilute solution of silver nitrate to the solution of the sodium salt prepared in the manner just described. The orange-red precipitate, after thorough washing on a plaited filter, was sucked dry in a Buechner funnel, pressed out on a porous plate, and dried *in vacuo* over calcium chloride, as it was found that these silver salts blackened if dried *in vacuo* over sulphuric acid. In silver determinations by the method of Carius, nitric acid alone was used, as the substance contains three atoms of bromine to one of silver.

[1] Work is now in progress at the Chemical Laboratory of the University of Minnesota, on the abnormal reaction of alkyl iodides on phenol silver salts, and also on the yellow potassium derivative of tribromoguaiacol.

[2] *Ann.*, 205, 66 (1880).

[3] *Ibid.*, 137, 208.

[4] *Ibid.*, 161, 340.

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Calculated for $C_6H_2Br_3OAg$: Br, 54.79; Ag, 24.7.
Found: Br, 54.12; Ag, 24.9.

It seemed necessary to confirm Purgotti's work by these analyses in order to establish beyond question that the two salts were isomers.

White Silver Salt of Tribromophenol.—Three methods have been discovered for converting the red salt into the white one. If a dilute solution of the sodium salt is heated to boiling and treated with a fairly dilute solution of silver nitrate, a pale orange precipitate appears at first, which on longer boiling and stirring gradually becomes white. A very slightly reddish specimen prepared in this way was washed thoroughly with water, then quickly with boiling alcohol, dried, and analyzed (I).

The second method consisted in forming the precipitate in very dilute solutions. It gave better results, but like the preceding, yielded in one operation not more than one gram. Moreover, the product in either case was apt to be contaminated with small quantities of the red isomer or of silver oxide. The third method gave a white product, and could be used with large quantities of material. It consisted in dissolving the freshly precipitated, well washed red salt in a little strong ammonia, diluting to about five times its volume to keep the rather insoluble ammonium salt from separating, and then adding dilute sulfuric acid till the solution was only faintly alkaline. A slight white precipitate was formed here, which was dissolved by adding more water, and then a concentrated solution of silver nitrate was added in small portions at a time until a precipitate begins to appear. If this was reddish, an attempt was made to whiten it by stirring it with the solution. If this did not succeed, strong ammonia was added drop by drop until the precipitate had turned white or was dissolved. In the latter case it was diluted again with water, and silver nitrate added, when a white precipitate appeared. After a white precipitate had been obtained, the addition of silver nitrate was continued with constant stirring until the reaction had come to an end. A specimen of salt prepared in this way was washed thoroughly and dried *in vacuo* over phosphoric anhydride for analysis II. The salt prepared in this way showed no trace of the red isomer, even under the microscope.

The methods described above had the disadvantage of starting from the red salt; this was avoided by the following process, which was, therefore, the most convenient, if large amounts were required. A few drops of ammonia added to the sodium salt led to the exclusive formation of the white salt. If sufficient ammonia was present to prevent an immediate red precipitate on the addition of silver nitrate, further slow addition with stirring produced a white precipitate or a reddish precipitate becoming white. If the red color was persistent, not enough ammonia had been added, and a drop or two more was used. The white salt was

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collected on a plaited filter for washing as it clogged the filter if suction were applied. When washed, it was sucked dry, and finally dried *in vacuo* over calcium chloride.

Calculated for $C_6H_2Br_3OAg$: Br, 54.79; Ag, 24.65.
Found: Br, 54.67, 54.48; Ag, 25.06, 24.66.

Silver Salt of the Monomethyl Ether of Tribromoresorcinol.—The monomethyl ether of resorcinol was made by the method of Tiemann and Parrisius.[1] It showed the boiling point 243–244°, and was then converted into the tribromo derivative as directed by the same authors. On adding silver nitrate to the solution of the sodium salt, prepared as in the case of tribromophenol, a distinctly yellow precipitate fell, which rapidly became white, especially if shaken with the liquid. The tendency to pass over into the white form was so great that we could not isolate the orange modification. The white salt was filtered, washed with distilled water, and dried *in vacuo* over calcium chloride for analysis. The dry salt is almost pure white.

Calculated for $C_6HBr_3(OCH_3)OAg$: Br, 51.27. Found, 51.10.

Silver Salt of Tribromoguaiacol.—Tribromoguaiacol was made by the method of Hill and Jennings.[2] An aqueous solution of the potassium salt was treated with silver nitrate solution, when a copious precipitate fell, yellowish red at first, but rapidly growing redder and more gelatinous, until it became as clear red and transparent as currant jelly. When an attempt was made to filter some of it immediately after precipitation, in this transparent stage the filter paper was clearly visible through the gelatinous mass. The transparent precipitate soon turned white and opaque, but if allowed to stay in the solution, this change was accompanied by a general decomposition, shown by blackening. Many schemes were tried without avail to isolate the red salt.

The white salt was obtained best by the ammonia method used in the case of tribromophenol, avoiding the appearance of the red salt. It was washed with a little very dilute ammonia, which seemed to prevent decomposition, perhaps by dissolving the finer particles, and finally with distilled water. It was dried *in vacuo* and analyzed for bromine.

Calculated for $C_6HBr_3(OCH_3)OAg$: Br, 51.27. Found, 51.22.

A Yellow Potassium Derivative of Tribromoguaiacol.—As it was desired to try to form the red silver salt in another solvent than water, acetone was chosen for this purpose. Some tribromoguaiacol was dissolved in dry acetone, and as potassium hydroxide is almost insoluble in it, a lump of this alkali free from halogen, weighing about a gram, was placed in the test-tube. Its corners had been previously rounded

[1] *Ber.*, 13, 2362 (1880).
[2] *Am. Chem. J.*, 15, 164.

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off by water, which had then been washed off with several amounts of dry acetone. No action was apparent at first, but on shaking, the solution became yellow, and yellow flakes were peeled off the lump of caustic potash. The solution was allowed to stand for awhile to allow any potash which might be contained in the flakes to react with the excess of tribromoguaiacol, and then the lump was removed, the flakes of salt filtered off, washed with dry acetone, dried over phosphoric anhydride, *in vacuo*, and analyzed.

	Calculated for		
	$C_6HBr_3(OCH_3)OK$.	$C_6HBr_3(OCH_3)OK.H_2O$.	Found.
Br	60.11	57.52	57.93
K	9.81	9.38	9.15

From these analyses it would appear that the substance contains one molecule of water of crystallization, or is an addition product of potassium hydroxide and tribromoguaiacol. Unfortunately, a direct determination of water could not be made as the compound decomposed very readily on heating. Analyses like these of a substance which could not be purified must be accepted with caution.

The addition of a little water to the yellow acetone solution of the salt or addition product causes an immediate decolorization. Water slowly dissolves the dry compound to a clear colorless solution from which carbon dioxide precipitates the tribromoguaiacol.

A saturated dry acetone solution of silver nitrate gives a red precipitate with the yellow solution of the potassium derivative, but all attempts at isolation of this precipitate, which we suspected to be identical with the red salt obtained in water solution, resulted in failure, owing to the very rapid blackening of the precipitate.

It is the intention of the junior author to pursue the study of this compound, with a view to proving its composition and investigating its constitution, as well as comparing it with the salt prepared in aqueous solution. It is also hoped that it may be found possible to prepare other compounds of like nature.

Silver Salt of Tetrabromoguaiacol.—Tetrabromoguaiacol was made by the method of Jackson and Torrey,[1] and its action tried. On adding the silver nitrate to its potassium salt, an immediate white precipitate was formed, which quickly turned red. The red product had the same appearance as the red silver salt from tribromoguaiacol, and went through the same changes; it became transparent and gelatinous, and then white and opaque, but it decomposed even more readily.

A pure white salt was obtained by the usual ammonia treatment, which could be washed free from silver without decomposition.

[1] *Proc. Am. Acad.*, 33, 165 (1898).

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Mercurous Salts of Phenols.

Mercurous Salt of Tribromophenol.—The sodium salt was precipitated by a slightly acid solution of mercurous nitrate. The yellow precipitate was washed with water till dilute hydrochloric acid gave no reaction for mercurous chloride in the filtrate, then as it contained tribromophenol it was boiled with alcohol, filtered, washed with cold alcohol, and finally with ether. It was dried *in vacuo* and analyzed for bromine. The dry salt was a full yellow.

Calculated for $C_6H_2Br_3OAg$: Br, 45.45. Found, 45.24.

A yellow salt, presumably identical with the one described here was precipitated when the acid mercurous nitrate solution was added to an alcoholic solution of the free phenol.

Mercurous Salt of Triiodophenol.—To a dilute alcoholic solution of triiodophenol, prepared by the method of Körner,[1] was added a slightly acid solution of mercurous nitrate. A very heavy granular orange-yellow precipitate fell immediately, which was filtered off, washed well with alcohol, brought to constant weight *in vacuo* over phosphoric anhydride, and analyzed. The dry salt was a deep orange-red.

Calculated for $C_6H_2I_3OHg$: I, 56.77. Found, 57.80, 57.22.

Mercurous Salt of Tribromoresorcinol. — A slightly acid solution of mercurous nitrate gave a heavy yellow precipitate with a dilute solution of tribromoresorcinol in alcohol. The precipitate was filtered off, washed with alcohol, dried *in vacuo* to constant weight, and analyzed. The dry salt had a full yellow color.

Calculated for $C_6HBr_3(OH)OHg$: Br, 43.94. Found, 43.56.

Under the same conditions, yellow precipitates were obtained from alcoholic solutions of tribromoresorcinol monomethyl ether and tetrabromoguaiacol.

Work on the Constitutions of the Two Salts.

Experiments were tried on the behavior of the two salts with iodine, bromine, chloroformic ester, chloroacetic ester, and acetobromoamide, $CH_3CONHBr$, without our obtaining any definit compounds, or being able to trace any differences in action between the two salts. Treatment with acids, alkalies, or zinc and acetic acid showed no perceptible difference. Acetic acid set free tribromophenol, recognized by its melting point, from each modification.

In trying the result of alkylation, no differences could be detected in the action of the two salts; the interesting observation was made that if undiluted ethyl bromide or diluted alkyl halides were used, the normal ethers appeared, but with dry, undiluted alkyl iodides the silver salts

[1] *Ann.*, 137, 213.

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were converted into amorphous compounds, which will be investigated more fully later. At present, just enough work has been done to show that the same compound was formed by all the iodides used, and that this reaction did not distinguish between the two salts.

Action of Ethyl Bromide.—Undiluted ethyl bromide was poured over the dry, white salt in an Erlenmeyer flask, and allowed to stand three days, with occasional shaking. It gave the known tribromophenetole, melting at 72–73°.

The same experiment on the red salt gave an identical result.

Action of Ethyl Iodide in Alcohol on the Salts.—Purgotti obtained the tribromophenetole from the red salt by ethyl iodide in alcohol.

Some of the white salt was treated with a mixture of one part of ethyl iodide to about two of alcohol. On slight warming, silver iodide formed, which was filtered off after standing three hours. Crystals were found by evaporation, which melted at 69–71.5° without purification. This is obviously the normal ether, tribromophenetole, and the white salt acts like the red.

Undiluted Ethyl Iodide on the Red Salt.—2.8 g. of red silver salt, dried over phosphoric anhydride, were covered with dried, freshly distilled ethyl iodide, in a stoppered flask, and the mixture well shaken during the whole experiment. At first no action could be observed, but after a time the salt appeared to darken, and then became a bright green, whereupon the liquid began to grow blue. When the solution was a bright blue, there was a sudden change in the somewhat voluminous greenish precipitate, which became yellow and curdy, having every appearance of silver iodide. The blue color of the solution immediately began to fade, and after a few minutes had turned to a light yellowish brown. The mixture was then allowed to stand about ten minutes, after which the precipitated silver salt was filtered off, and washed well with dry chloroform, in which the reaction product was known to be soluble. Upon adding 95 per cent. alcohol to the filtrate, a white powdery precipitate was produced which, after drying, commenced to shrink at 260°, and sintered and decomposed between 270° and 290°.

This amorphous precipitate was purified for analysis by repeated solution in chloroform and precipitation by alcohol, as it had been found that evaporation of the solution deposited the substance in the form of a varnish.

One fraction, air-dried only, was analyzed.

0.1535 g. gave 0.2312 g. AgBr = 64.10 per cent. Br.

Another fraction was dried by heating an hour at 100–110°, and standing over phosphoric anhydride.

0.1538 g. gave 0.2315 g. AgBr = 64.05 per cent. Br.

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The silver salt from the analysis was shown to contain no iodine.

The filtrates from this compound yielded needles, estimated at less than a decigram in amount, which gave the melting point of the normal ether. It is indeed surprising that such a small percentage of the tribromophenetol should be formed by this reaction.

Action of Undiluted Methyl Iodide on the Red Salt.—Methyl iodide under the same conditions gave an identical action, noticeably slower than with the ethyl iodide. It was allowed to stand two hours, though apparently complete long before this, and was worked up in the same manner. The product was identical in appearance with that from ethyl iodide, and analysis showed it to have the same halogen content:

0.1545 g. gave 0.2323 g. AgBr = 63.98 per cent. Br.

Action of Allyl Iodide on the Red Salt.—The allyl iodide used was freshly distilled and, when used, was nearly colorless. In this case the reaction was very vigorous when started, so the red salt was moistened with a little dry benzene, and after pouring off all that was possible, the allyl iodide was added. The action was apparently identical, but a rather poor yield of the amorphous compound was obtained, possibly on account of the presence of the benzene.

0.0822 g. gave 0.1244 g. AgBr = 64.40 per cent. Br.

Action of Methyl Iodide Undiluted on the White Salt.—The phenomena observed were identical with those with the red salt. The amorphous substance was isolated and analyzed.

0.1564 g. gave 0.2328 g. AgBr = 63.34 per cent Br.

Although this result is over 0.6 per cent. lower than that from the red salt, there is little doubt that the products are the same.

Hantzsch had already shown in his paper that the normal ether was given by both the red and white salts, on treatment with methyl iodide diluted with ether.

Tribromoresorcinol Dimethyl Ether.—This compound, hitherto undescribed, was chosen to try the behavior of diluted methyl iodide on the white silver salt of tribromoresorcinol monomethyl ether. The salt was treated with the mixture of methyl iodide and alcohol on the steam bath with a reflux condenser, till the action apparently ceased.

The filtered solution was then heated again and water added till the precipitate barely dissolved, when cooling gave a powdery precipitate which became crystallin on scratching and stirring. It was recrystallized in the same way from alcohol and water to the constant melting point 68–69°; insoluble in water and alkalies, soluble in alcohol, ether, acetone, benzene, ligroin.

Calculated for $C_6HBr_3(OCH_3)_2$, 63.81. Found, 63.95

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WYOMING.]

ANALYSIS OF ZYGADENUS INTERMEDIUS.

(FIRST PAPER.)

BY FRED. W. HEYL AND L. CHAS. RAIFORD.

Received November 28, 1910.

The poisonous character of the several species of plants designated as death camas has long been known to the stockmen of certain western states. These plants belong to the genus *Zygadenus* and are found in Montana, Wyoming, Colorado, and other states of the Northwest, where they have from time to time[1] caused heavy stock losses, particularly among sheep.

In Wyoming the most common species is the *intermedius*, and the greatest stock losses noted have usually occurred in the early spring when this plant is in bloom, and before ordinary forage plants are plentiful. In addition to this, there prevails the idea that poisoning is more frequent immediately after rain-storms and it has been suggested that this might be accounted for on the general knowledge that in some plants the active constituent is found chiefly in the roots,[2] and that when the ground is moist and soft the bulbous portion could be more easily uprooted by cattle. Such a view, however, is scarcely supported by our experiments, for analyses show that the bulb and the leaf differ but little in the amount of alkaloid contained. It will be shown that the flower contains a higher percentage of alkaloid than any other part of the plant. In the light of these facts the more probable explanation of the greater frequency of poisoning immediately after rain-storms would seem to be that at such a period either the flowers are more numerous, or the animal then eats a greater quantity of the leaves than usual. A possible explanation of the tendency to eat such a plant at all when anything else is available, at which some surprise has been expressed, may be found in the fact that the plant as a whole has a relatively high food value, while the bulb, which is doubtless eaten to some extent, contains a high percentage of sugar.

A knowledge of the constituents of the several species of the genus *Zygadenus*, or of the details of the behavior of animals subjected experimentally to their influence, is confined to a report of a study of the stock-poisoning plants of Montana, by Chesnut and Wilcox[3] who conducted feeding and other experimental tests with extracts of *Zygadenus venenosus;* and to a preliminary chemical study of the constituents of the same species

[1] Chestnut and Wilcox, Div. Bot., U. S. Dept. Agr., *Bull.* 26, 34 (1901).

[2] Blankinship, Montana Exp. Sta., *Bull.* 45, 91 (1903), states that the bulb of death camas is the most poisonous part of the plant, but his statement is not supported by experimental evidence.

[3] *Loc cit.*

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by Slade.[1] The latter obtained, by means of the color tests described by Merck,[2] and Wright and Luff,[3] evidence which led him to conclude that the poisonous character of the plant is due to the presence of the alkaloids sabadine, sabadinine, and veratralbine.

The present paper reports the results of the proximate analyses of the different parts of the species available in Wyoming. In the preliminary work, various methods have been used in securing the alkaloid with a view of subsequently isolating a larger quantity by the method found most suitable. We shall report later upon the properties of this and other constituents obtained.

Experimental Part.

Preparation of Material.—Portions of *Zygadenus intermedius* which together weighed 5 kilograms in the green state were collected between May 26 and June 2, 1910. The first lot consisted of plants that had not reached the flowering stage, while the last contained many plants with flowers, though the latter were not mature. In preparing for analysis the leaves and flowering tops were separated from the bulbs, and the latter in all cases deprived of the outer layer and the roots. The average weight of the plant was 7.4 grams, and moisture determinations at 95–100° showed losses of 75.50 per cent. and 68.93 per cent. on the leaves and flowering tops, and on the bulbs and roots, respectively. The various parts were allowed to dry in the air at a somewhat elevated temperature, under which conditions the leaves dried readily, while the bulbs long remained sticky and had to be sliced. Six weeks were required to dry them to such a state that they could be ground easily. The grinding and sieving necessitated the shielding of one's face in order to avoid the extremely irritating dust, the character of which was probably due to one or more of the sternutatory veratrum alkaloids, possibly veratralbine.

The investigation was begun by extracting separate portions of 2 grams each in a Soxhlet apparatus with ligroin, ether, and alcohol, respectively. The quantities removed are given in percentages in Table I.

TABLE I.

Extract.	Leaf.	Flower.	Bulb.	Root.
Ligroin extract (dried at 93°)	2.04	2.80	0.62	0.89
Ether extract, total	5.47	5.21	3.18	3.05
Ether extract, volatil (110°)	1.33	1.07	1.30	0.80
Alcohol extract (dried at 110°)	35.12	46.27	39.60	lost

The proximate analyses were conducted in accordance with the usual[4] methods, and gave the results stated in Table II.

[1] *Am. J. Pharm.*, 77, 262 (1905).
[2] *Arch. Pharm.*, 229, 164 (1891).
[3] *J. Chem. Soc.*, 35, 415 (1879).
[4] U. S. Dept Agr., Bur. of Chem., *Bull.* 107 (Revised).

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TABLE II.

	Leaf.	Flower.	Bulb.	Root.
Moisture	6.91	6.13	7.50	7.56
Starch by diastase	absent	absent	23.53	absent
Pentosans	10.81	7.95	4.41	12.04
Crude fiber	16.17	10.58	5.08	21.53
Protein	13.25	19.73	6.19	6.78
Ash	8.12	8.91	4.29	18.41

The material removed by extraction with alcohol, the amounts of which were given in Table I, was examined for resin (insoluble in water), for sucrose and hexose sugars. The results are given in Table III, to which have been added the figures representing the dextrin determinations.

TABLE III.

	Leaf.	Flower.	Bulb.	Root.
Resin	5.03	undet.	2.58	5.00
Sucrose	5.60	undet.	18.44	1.02
Reducing sugar[1]	5.89	undet.	6.69	2.45
Dextrin	3.26	trace	1.40	0.34

Determination of Alkaloid in the Leaf.—The presence of an alkaloid in the leaf having been detected by a preliminary assay, it was decided to make determinations in more than one way. Accordingly, portions of leaf were next assayed by three different methods, as follows:

I. The first method[2] tried is that official in the United States Pharmacopeia for the assay of belladonna leaves, which we modified to the extent of using ether instead of chloroform in the final extraction. Duplicate determinations in this way gave crude alkaloidal residues weighing 0.0883 and 0.0910 gram, which required for neutralization 1.13 and 1.07 cc., respectively, of 0.1 *N* sulfuric acid.

The residues so obtained, which were contaminated with conspicuous amounts of resin that was insoluble in dilute acid, were united, the mixture acidified and filtered, and the clear filtrate precipitated with Mayer's reagent. The insoluble mercury compound that resulted was collected on a filter, washed with water, suspended in dilute sulfuric acid, and decomposed by hydrogen sulfide. After standing over night the mixture was filtered, the mercuric sulfide washed with water, the filtrate made alkaline with ammonia and extracted with ether. Evaporation of the ether left a crystallin alkaloidal residue that weighed 0.0815 gram, and which corresponded to 0.41 per cent. of the drug employed. The combined, partially exhausted drug residues obtained in the first part of the operation were next exhausted by percolation with 5 per cent. sulfuric acid. The percolate was made alkaline with ammonia, and worked up for alkaloid in the usual way. A further quantity of alkaloidal residue

[1] Calculated as invert sugar.

[2] Given in detail in U. S. Disp., 19th Ed., p. 228.

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weighing 0.0230 gram and requiring 0.11 cc. 0.1 *N* acid for neutralization, was obtained.

II. A second portion of leaf weighing ten grams was assayed by the method specified above and modified to the extent of using Prolius'[1] solution instead of the ether-chloroform mixture as a menstruum. The crude alkaloidal residue obtained by this method weighed 0.0807 gram, and required 1.04 cc. 0.1 *N* acid, and 0.78 cc. Mayer's reagent. Decomposition of the mercury salt in the manner already described gave 0.0280 gram of crystallin residue, representing 0.28 per cent. of the original material. Further percolation of the partially exhausted drug with 5 per cent. sulfuric acid yielded an alkaloidal residue that weighed 0.0107 gram and sufficient to neutralize 0.10 cc. 0.1 *N* acid.

III. A third portion of leaf weighing 40 grams was exhausted as far as possible by repeated extractions with boiling 95 per cent. alcohol. The extract was then concentrated under reduced pressure to a volume of 200 cc., the dissolved solids determined in an aliquot of 5 cc., and the remainder poured into a mixture of 40 cc. *N* sulfuric acid, and 460 cc. water. A brown, resinous mass amounting to 4.9 per cent. of the weight of the drug was precipitated. This was collected on a filter and washed with dilute acid.

The acid filtrate was now made alkaline with ammonia, and worked up for alkaloid in the usual way. The crude residue obtained weighed 0.2382 gram, and required for neutralization 3.70 cc. 0.1 *N* acid, and for precipitation 7.49 cc. Mayer's reagent. The residue was known to be contaminated with resin, and in order to correct for this the mercury compound was decomposed as described above, and a crystallin alkaloid obtained. The latter weighed 0.1033 gram, and represented 0.26 per cent. of the drug.

The residue of leaf left after extraction with alcohol was percolated with 5 per cent. sulfuric acid until the percolate no longer reacted with Mayer's reagent. A further yield of alkaloid amounting to 0.0139 gram and neutralizing 0.18 cc. 0.1 *N* acid was secured.

Determination of Alkaloid in the Bulb.—When three separate portions of ten grams each of the bulb were subjected to the process designated as I under the leaf, there were obtained crude alkaloidal residues that weighed 0.0560, 0.0530, and 0.0450 gram, and which neutralized 0.32, 0.34, and 0.36 cc., respectively, of 0.1 *N* acid. As with the leaf, the partially exhausted drug residues from twenty grams were percolated to exhaustion with 5 per cent. sulfuric acid, and the percolate yielded 0.0168 gram crude alkaloidal residue that neutralized 0.13 cc. 0.1 *N* acid, and precipitated 0.37 cc. Mayer's reagent.

II. Two ten-gram portions of bulb were assayed in accordance with

[1] Alcohol 8 cc., ether 88 cc., ammonia (10 per cent.) 4 cc.

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method II outlined under the leaf and gave impure alkaloidal residues weighing 0.0876 and 0.0770 gram, equivalent to 0.97 and 0.96 cc. 0.1 *N* acid, and 1.90 and 1.51 cc., respectively, of Mayer's reagent. Decomposition of the mercury salt of the first of these in the usual way gave 0.0390 gram of crystallin residue, equivalent to 0.39 per cent. of the drug.

III. Fifty grams of bulb were exhausted as nearly as possible by repeated extraction with boiling 95 per cent. alcohol. When the first portion of the extract, measuring 500 cc., was concentrated, it deposited crystals of sucrose. The combined extracts were then concentrated under reduced pressure to a small bulk and finally allowed to dry out over sulfuric acid in a desiccator. The residue was next boiled with 150 cc. 95 per cent. alcohol and the undissolved portion (which had a sticky consistency) removed and boiled with a second portion of alcohol. The final residue which was granular in character weighed 3.771 grams and represented 7.54 per cent. of the bulb. When heated upon platinum foil the substance produced caramel; tested with Fehling's solution, it showed slight reduction. Examined with the polariscope it showed the constants for cane sugar mixed with a trace of reducing sugar. The specific rotation found was $[\alpha]_D = +62.70$ at 20°, while that for the pure sucrose is +66.48.

The alcoholic extract obtained above, which had a strong reducing action on Fehling's solution, was now concentrated to the consistency of a fluid extract, and then diluted with a mixture of 10 cc. *N* sulfuric acid and 240 cc. water. A brown, flocculent resin precipitated. This was collected on a filter, washed with water and dried. It weighed 1.2875 grams and was equivalent to 2.58 per cent. of the bulb.

The acid filtrate obtained above was now shaken repeatedly with ether, which removed a brown tar, weighing 0.2922 gram, equivalent to 0.58 per cent. The liquid was then made alkaline with ammonia, and the alkaloid removed by extraction with ether as already described. From the ether the alkaloid was recovered by shaking out with sulfuric acid in the usual way. The liquid obtained was made alkaline with ammonia a second time, extracted with ether and the latter evaporated off. The residue weighed 0.0905 gram, was completely soluble in 0.1 *N* acid, of which 1.10 cc. were required for neutralization, and 2.90 cc. of Mayer's reagent for precipitation.

It was found in the determination just specified that ether failed to remove all the alkaloid from the second ammoniacal liquid. A further extraction with chloroform yielded 0.0307 gram of alkaloid that required 0.23 cc. 0.1 *N* acid, in which it was completely soluble, and 1.30 cc. Mayer's reagent for precipitation. The combined alkaloidal residues constitute 0.24 per cent. of the bulb.

The flower and root were next assayed by the method designated above

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as I. Duplicate determinations on ten-gram portions of the flower gave crude alkaloidal residues weighing 0.1358, and 0.1842 gram, which required 1.82 and 2.32 cc. 0.1 *N* acid for neutralization, and 3.79 and 3.60 cc., respectively, of Mayer's reagent for precipitation.

Assays of duplicate portions of the root in the same way gave crude alkaloidal residues weighing 0.0504, and 0.0422 gram. These required for neutralization 0.52, and 0.56 cc. 0.1 *N* acid, and 1.15, and 1.15 cc., respectively, of Mayer's reagent for precipitation.

The work will be continued in this laboratory.

LARAMIE, WYOMING.

[CONTRIBUTION FROM THE DEPARTMENT OF PLANT AND ANIMAL CHEMISTRY, MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION.]

THE SOLUBLE CARBOHYDRATES IN ASPARAGUS ROOTS.

BY FRED W. MORSE.

Received November 17, 1910.

This paper is a simple statement of progress in a study of the composition of the asparagus plant, and is part of an investigation of the fertilizer requirements of asparagus now being conducted at this agricultural experiment station.

The nutrition of asparagus shoots in early spring necessarily depends on the material stored in the roots, since the mode of growth of the young shoots up to the time of cutting for the table renders assimilation from the atmosphere nearly impossible. Hence, roots were selected as the first portion of the plant to be studied.

A search of the literature of asparagus failed to show anything about the composition of the roots, beyond a few scattering ash analyses and a brief article by Vines[1] on the reserve proteins.

Very recently, however, Wichers and Tollens[2] have reported an extensive study of asparagus roots, and called attention to similar work by Tanret,[3] brief abstracts of whose articles had been overlooked.

Since the work has been wholly independent of that just mentioned, it is believed that this report of progress will be of value at this time.

All the material for the work here reported was prepared ni other divisions of the department, and consisted of finely pulverized samples of individual root systems. All of the plant below the surface had been dug up, freed from earth and dried at about 50°. The roots were secured in November of the second year after setting when translocation from the tops was believed to be complete. For subsequent study of the effects

[1] *Proc. Roy. Soc. London*, 52, 130–2. Abstr. *J. Chem. Soc.*, 64, 431.

[2] *J. Landw.*, 58, 101–16.

[3] *Bull. soc. chim.*, [4] 5, 889, 893. *Compt. rend.*, 149, 48–50. Abstr. *J. Chem. Soc.*, 1909, 634. *C. A.*, 3, 2677.

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of different fertilizers, the individual samples were separately analyzed; but for this report detailed results are unnecessary.

The average proximate composition of the dry matter of 16 roots was as follows:

Protein (nitrogen × 6.25)	11.03 per cent.
Fat	1.00 per cent.
Fiber	15.39 per cent.
Nitrogen-free extract	66.34 per cent.
Ash[1]	6.24 per cent.

The proximate composition showed clearly that the soluble non-nitrogenous matter included most of the reserve material of the roots.

The methods of the Association of Official Agricultural Chemists[2] for sugars, starch, pentosans and galactans were employed for estimating the different carbohydrates in the reserve material.

An examination of 25 roots showed 12 to contain no reducing sugars while most of the others had only traces present; therefore, reducing sugars were not estimated but reckoned with total sugars. The latter were especially abundant and ranged from 26.4 per cent. to 50.8, only 2 samples containing less than 35 per cent. calculated to dry matter.

Pentosans were determined in 16 samples and ranged from 7.32 per cent. to 10.68 per cent. in the dry matter. Galactans were determined in 4 individual samples and in a composit sample, but were insignificant in amount, averaging only 1.04 per cent.

In the estimation of starch by the diastase method, it was found that there was no more glucose obtained than was accountable from the diastatic extract. Subsequent examination revealed it in only microscopic traces. Six different samples, after having undergone the diastase treatment as for starch, were filtered and washed, and the residues then subjected to 2 hours' boiling under reflux condensers, with 100 cc. of hydrochloric acid of approximately 6 per cent. After cooling the solutions they were nearly neutralized with sodium hydroxide, and made up to 250 cc. The reducing sugars were then determined by Fehling's solution and the weights of copper calculated to glucose. The 6 samples averaged 8.6 per cent. of glucose by this hydrolysis; but since the same samples averaged 8.67 per cent. of pentosans reckoned from furfural-phloroglucide, it is improbable that there are any hydrolyzable carbohydrates unaccounted for by the usual analytical methods.

From these different analyses it was found that the dry matter of 16 roots contained:

Sugars calculated as invert sugar	41.43 per cent.
Pentosans	8.78 per cent.
Galactans	1.04 per cent.

[1] Ash determinations were made in the fertilizer division of the department.

[2] U. S. Dept. Agr., Bur. of Chem., *Bull.* 107, 38–56.

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The carbohydrate forming over 40 per cent. of the dry matter was at first assumed to be sucrose. The analytical procedure had shown it to be soluble in cold water and inactive to Fehling's solution until hydrolyzed, which was easily accomplished by dilute acids. Repeated attempts to recover sucrose by means of strontium hydroxide[1] resulted in securing only very small quantities of a straw-colored sirup which could not be crystallized like sucrose, but did not reduce Fehling's solution.

Methyl alcohol was found to extract considerable quantities of the sugar from the roots, which suggested raffinose; but no mucic acid could be obtained by oxidation with nitric acid, although a parallel test with lactose under the same conditions yielded it in abundance.

Osazones were prepared from both methyl alcohol and water extracts, before and also after inversion. The characteristic yellow, crystallin precipitate was easily obtained in every case. Five such precipitates had their melting points determined and they ranged between 203 and 210° and were accompanied by an evolution of gas. Glucosazone was evidently the only one formed.

About 100 grams of roots were extracted by cold water and the extract concentrated on the water-bath to a thick, black, tenacious sirup, which was strongly reducing to Fehling's solution. Heat and probably acid salts had brought about a nearly complete hydrolysis during the evaporation. This extract failed to yield mucic acid, but oxalic acid was readily formed.

Portions of the sirup were subjected to distillation with hydrochloric acid of 1.06 sp. gr. and yielded a small quantity of furfural. The furfural-phloroglucide, after being dried and weighed, was found to lose about two-thirds of its weight by solution in hot 93 per cent. alcohol, indicating that it was largely methyl-furfural.

The action of polarized light was observed upon freshly prepared water extracts of two different roots, and upon three sirups which had been fractionated by strontium hydroxide. The solutions were clarified by lead subacetate and the readings were made in a Schmidt and Haensch triple-shade saccharimeter through a 200 mm. tube. The solutions were then inverted and again polarized together with two solutions of the dense water extract above mentioned.

Subsequent to the readings, the actual strength of sugar in each solution was determined with Fehling's solution. The solutions were necessarily dilute, because the roots on moistening swelled to a large volume and small charges had to be used. The three sirups were small in amount as before mentioned, and the black sirup from the water extract was difficult to clarify to a point where light would pass through it.

[1] E. Schulze, *Z. physiol. Chem.*, 20, 513–5.

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POLARIZATION BEFORE HYDROLYSIS.

	Sugar in 100 cc. Grams.	Saccharimeter reading.	Sp. rotatory power.
Root 34	1.738	+ 0.5	+ 5°
Root 40	2.259	— 1.4	— 10°
Sirup A	2.623	+ 2.88	+ 18.9°
Sirup B	2.775	— 1.6	— 10°
Sirup C	0.858	zero	zero

POLARIZATION AFTER HYDROLYSIS.

	Invert sugar in 100 cc. Grams.	Saccharimeter reading.	Sp. rotatory power.
Root 34	0.893	— 2.33	— 45°
Root 40	1.189	— 4.10	— 59°
Sirup A	1.381	— 3.45	— 49°
Sirup B	1.461	— 5.25	— 62°
Sirup C	0.452	— 1.3	— 49°
Extract 1	0.936	— 3.0	— 55°
Extract 2	2.350	— 7.8	— 57°

The action on polarized light both before and after inversion excludes the possibility of the carbohydrate being pure sucrose, while the failure to secure it with strontium hydroxide renders its absence probable.

Fructose was clearly demonstrated by the osazone and the negative optical activity, also by fine reactions with resorcinol and hydrochloric acid. Glucose is indicated by the osazone and the fact that the specific rotatory power of the inverted solutions is not high enough for pure fructose. Fructose clearly predominates over the glucose, and the non-reducing property before hydrolysis indicates some condensation product formed between them. The behavior of individual root extracts does not ponit to any fixed proportion of the two sugars.

These results are, on the whole, in close agreement with those of Wichers and Tollens. There was, however, a marked difference in the behavior of the water extract of the roots, which contained the sugar-like carbohydrate. Wichers and Tollens used boiling water and state that only a portion of this carbohydrate was soluble in water when extractions were made on the water bath. Their solutions also reduced Fehling's solution before hydrolysis.

My extractions were all made with water at 20° and, until hydrolyzed, either had no reducing action or precipitated no more than traces of copper.

This difference in solubility and reducing action is doubtless due to the stage of development of the roots, since Wichers and Tollens worked upon roots gathered in April and July instead of in November.

Tanret isolated two distinct crystallin carbohydrates from the root sap, one of which had a rotation of —35.1° and the other +30.3°.

Sirups A and B fractionated with strontium hydroxide showed opposit

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rotations before inversion, but lack of material has given no opportunity to confirm further his observations.

Grateful acknowledgment is made of suggestions received from Dr. Joseph B. Lindsey during the progress of this investigation.

AMHERST, MASS.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

FASTING STUDIES: I. NITROGEN PARTITION AND PHYSIOLOGICAL RESISTANCE AS INFLUENCED BY REPEATED FASTING.[1]

BY PAUL E. HOWE AND P. B. HAWK.

Received November 26, 1910.

Historical.

The literature upon fasting is large and may be divided into two classes, that presenting data upon (*a*) simple fasts of (1) short duration, and dealing with changes in body weight, nitrogen partition, the blood, temperature, secretions, and the effect of drugs, or only as a preparation for the study of normal or pathological metabolism; (2) more or less profound fasts, which include in addition to those changes mentioned above, losses in the weight and differences in composition of the organs as compared to the normal organs; and (*b*) repeated fasts in which (1) the object was to study the effect of repeated fasting; or (2) fasts in which the main object was not the study of repeated fasting, but in which the subject was used repeatedly in various investigations, no regard being given to the original conditions, such as body weight, nitrogen equilibrium, etc.

Experiments on Repeated Fasting.—Investigations upon fasting have been limited mainly to the lower animals, while those upon repeated fasting are confined entirely to them unless the fasts of Succi[1] are to be considered as repeated fasts, which is hardly proper, since each fast was conducted under different circumstances as regards original condition, body weight, time of year, climate, etc.

Repeated fasts have been conducted upon dogs by Albitsky.[3] His investigations were made upon four dogs, two fasting absolutely, *i. e.*, without water, to a loss in body weight of 40.4 per cent. and 37.6 per cent., in twenty-nine days, and fifteen days respectively, and the second time with water *ad libitum*, with a loss of 53.2 per cent. and 45.8 per cent. in fifty-one and thirty days, respectively. The other two dogs fasted first

[1] The expense of this research was borne by the Department of Animal Husbandry of the College of Agriculture. It was presented in abstract at the Boston meeting of the Society of Biological Chemists. It was also presented by Mr. Howe to the Graduate School of the University of Illinois, in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

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with water, to losses of 41.5 per cent. and 38.7 per cent. in thirty-four days and twenty-five days, respectively, and the second fast to a loss of 43.7 per cent. and 49.0 per cent. body weight, in thirty-two days, and thirty-eight days respectively. Positive conclusions cannot be drawn from Albitsky's results. No study was made of the effect of a properly controlled repeated fast, either complete or with water. Hence he had no basis upon which to compare the effect of water upon the length of a fast. A study of the results show in general that water seems to lessen the breakdown of the body tissues, for in three out of the four cases the dogs fasted a greater length of time for the same loss in body weight when they received water than when no water was given.

Tuvim[4] subjected two dogs to three repeated fasts of three days each, the first fast being absolute, and the two following with a large water ingestion. A third dog was fasted but twice, the first fast being absolute and the second with water. His experiments were to study the effect of water upon fasting, and only the respiration data were observed. His results did not show that water had any pronounced effect upon the gas interchange, and no data are presented which would show the effect of repeated fasting upon the nitrogen partition.

Schulz working with Mangold,[9] Stübel[10] and Hempel[11] reports results upon repeated fastings in dogs. One dog weighing 16.1 kilograms was fasted for thirty-two days, when the premortal rise seemed to have set in, and then the animal was fed an insufficient nitrogenous diet for nine days, during which time it stored 23 grams of nitrogen. This nitrogenous feeding was followed by a seven-day carbohydrate feeding period with a loss of 12.93 grams of nitrogen, leaving a storage of 10.07 grams of nitrogen for the sixteen days, during which the animal was fed. This feeding period was followed by another fast of fourteen days with a further loss of 27.61 grams of nitrogen over that gained and lost during the feeding.

This same dog was subjected to a similar experiment one month later. At the beginning of this experiment the animal weighed 19.6 kilograms and probably had greater fat stores than in the first experiment. The dog was fasted for twenty-seven days, at the end of which time he was so reduced in strength that they feared he would die. Schulz described the condition as a collapse. Food was given, 400 cc. of milk on the first day and 300 grams of meat per day for four days, restoring the dog to a satisfactory condition, after which the dog was fasted further for sixty-one days, at the end of which time the animal was very weak, although no premortal rise had occurred. During this second series of fasts the dog had lost 208.4 grams of nitrogen without regard to the nitrogen balance of the feeding period, while in the first series of fasts the dog lost 183.2 grams of nitrogen. The daily average nitrogen excretion

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during the second part of the first series and the first part of the second series was less than that in the first fast, while the average nitrogen excretion in the final fast of sixty-one days was even lower than the nitrogen excretion of the feeding period when sugar was ingested.

Stübel,[10] working on another dog, obtained a similar lowered nitrogen excretion after a short feeding period in which the dog received an insufficient food supply.

Manassein[5] reports experiments upon the repeated fasts of three rabbits in absolute fasting, and Albitsky[3] upon nine rabbits fasting either absolutely or alternately with water. In Albitsky's experiments the object was the study of the effect of water upon fasting and the following conditions were in force in his work. The first three rabbits were fasted absolutely while the remaining six rabbits were fasted alternately with and without water. The fasts were continued to a loss of 40 per cent. of the body weight and it was found that with each succeeding fast there was a tendency toward a decrease in the daily loss in body weight. Albitsky also observed that the recovery was slower with each succeeding fast and that as a result of fasting the animals' "oxidative" properties were increased so that from one to one and one-half times as much food and twice as much water were needed to keep the animal in a state of constant body weight. Pashutin[2] concludes from the work of these men that with the ingestion of water there is a slower loss in body weight than would occur in absolute fasting. The conditions of experimentation were not controlled accurately in these experiments and only general deductions may be drawn from the results.

Kagan[6] conducted experiments in repeated absolute fasting upon pigeons and showed in the birds results similar to those obtained upon dogs and rabbits, *i. e.*, a slower loss in body weight upon repeated fasting. This decrease in the loss of body weight does not continue with each succeeding fast but remains fairly constant. Albitsky[3] reports results upon pigeons which confirm his findings upon rabbits. He also gives data showing the influence of water upon fasting.

Ugrumoff[7] in two experiments upon pups showed that water exerted a sparing influence upon the organs over the loss found by fasting when a salt solution was given. Sadoven[8] working along the same lines subjected rabbits to repeated fasts under varying conditions such as absolute, with water, or with salt solution. He showed that salt solution exerted a sparing influence upon the loss of body weight as compared with complete fasting, while water exerted a still greater influence.

Bischoff and Voit[13] made a number of fasts, twenty-eight, upon one dog, under widely varying conditions, no single fast being more than eight days long and some were for only one to two days.

Seeland[14] conducted experiments on short repeated fasts with pigeons

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and roosters and showed that those birds which were subjected to repeated fasts of one to three days' duration gained weight more rapidly, their tissues were more solid, and the birds hardier and stronger than the control birds which were fed every day.

Richet[15] fed and fasted rabbits alternately in periods of six days; under such treatment they died in about a month and a half. Dogs subjected to a similar treatment lived about six months.

The work upon repeated fasting which has been cited cannot be interpreted in any way to show the effect of repeated fasting with water. The only cases in which the animals were fasted repeatedly and absolutely were those of Albitsky's rabbits which were fasted to a loss of 40 per cent. of the body weight. The most of the data presented deal largely with the changes in body weight. In some cases the respiration data, urine volume, P_2O_5 and urea excretion were determined but no accurate data are presented upon nitrogen partition.

Short, repeated fasts upon men are reported by Bucker,[16] Smith,[17] Ranke,[18] Pettenkofer and Voit,[19] Oppenheim,[20] Sadoven,[21] and Richet.[22]

Accurate studies of the nitrogen partition in fasting dogs have been made but recently. Previous to the advent of Folin's[32] method for creatine and creatinine no accurate investigations were made showing the nitrogen partition further than urea and ammonia, and in one or two cases the excretion of some of the pathological constituents of the urine.

Osterberg and Wolf[33] report the nitrogen partition in an experiment in which a dog was fed a low protein diet for a number of days and was then given a large amount of casein, after which the animal was fasted. Their findings cannot be considered normal nitrogen partition data for a fasting dog, inasmuch as the ingestion of a large amount of protein following a low protein diet would influence the nitrogen partition of the succeeding fasting days. Underhill and Kleiner[34] report findings upon the nitrogen partition in the urine of a fasting dog. Their experiment extended over a period of fourteen days, water being taken in varying amounts. Their results upon the nitrogen distribution during fasting as compared with a well fed animal show (1) "A slightly increased percentage of ammonia nitrogen and a correspondingly diminished urea percentage." (2) "The total creatinine nitrogen does not bear a strict relation to the total nitrogen"....."nor is the quantity excreted constant." "The relatively large output of creatin is also of special interest although its significance at this time is obscure." They report the presence of allantoin in the urine and also allantoin crystals in the urine after standing, and hold that the presence of this substance in "the urine of starving dogs shows without question that allantoin may have an endogenous origin." With regard to the purine and allantoin excretion

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they say that: "In inanition no fixed relationship appears to exist between the excretion of purine and allantoin."

Schöndorf,[35] working with a fasting dog, shows that the percentage of urea nitrogen may fall as low as 75 per cent. of the total nitrogen.

Leffmann[36] reports results which show that the creatine and creatinine excretions are fairly constant for animals of equal body weight, and that creatine or creatinine ingested with food, by a well-nourished dog, are seemingly excreted as such. Weber[37] shows that in fasting dogs as a result of muscular activity creatinine is excreted, while with uniformly nourished animals creatinine diminishes. Dorner[38] showed that fasting had no influence upon the excretion of creatinine in rabbits but that creatine appeared in increasing amounts. Böhtlingk[39] gives results upon the nitrogen distribution in fasting cats and rabbits.

The more recent work upon fasting which deals with the occurrence of creatine and creatinine has been presented by van Hoogenhuyze and Verploegh,[40] Benedict,[41] Benedict and Diefendorf,[42] and Cathcart,[43] who report results which are in general quite similar, the creatine remaining fairly constant, with a slight decrease as the fast progresses. The appearance of creatine in increasing amounts is reported by all except van Hoogenhuyze and Verploegh, who did not determin creatine. Benedict and Diefendorf report a decrease in creatine after the rise.

Results upon single prolonged fasts in the case of dogs have been reported by the following investigators: Howe, Mattill and Hawk,[23] Falck,[24] Kumagawa and Miura,[25] Pflüger,[26] Daddi,[27] Grandis,[28] Krawkaw,[29] L'abbé and Vitry[30] and Luciani and Bufalini.[31] The longest normal single fast has been reported by Howe, Mattill, and Hawk.[23] In this prolonged fast the animal fasted 117 days, during which time he received a constant water ingestion. The next longest normal fast upon which data are presented was reported by Falck.[24] This fast was continued for 60 days. Kumagawa and Miura[25] report a fast of 98 days during which time the dog was subjected to repeated doses of phlorhizin. This fast cannot be compared with true fasts because the phlorhizin introduces unknown factors.

Description.

Purpose and Plan.—The purpose of this investigation was to study the effect of repeated fasting upon the nitrogen partition in the urine of a dog. Changes in body weight were also observed. As a basis of comparison the nitrogen partition of the urine was determined during a normal feeding period for a number of days preceding the fast.

The plan of the experiment was as follows: The dog was brought into nitrogen equilibrium and then permitted to fast, the fast continuing until the inception of the premortal rise. At this time the animal was fed, the feeding continuing until the dog had regained its original body

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weight and was again in nitrogen equilibrium. Following this came the second fast.

Subject.—The animal used in this experiment was a small fox-terrier bitch, from one to two years old and weighing 3.41 kilograms (see Table V, p. 252). She was in good physical condition, well muscled, and had a medium layer of fat under the skin. Life in the experimental cage did not seem to annoy her in any way.

Articles of Diet: Meat.—The meat fed was beef, which had been prepared according to the method proposed by Gies[44] and modified by Hawk.[45] This method of preparation and preservation consisted in freeing the meat from as much visible fat and connective tissue as possible. The trimmed meat was ground three times in a sausage mill, using a smaller plate each time. The meat was passed through the mill and mixed thoroughly between each grinding. This insured a uniform sample. After the juices had been pressed out of the meat, it was sampled and then wrapped in paraffin paper in cakes of about 400 to 600 g., placed in a museum jar, frozen and kept in cold storage. This method of preservation was very satisfactory. The meat remained sweet, and after a period of six months the composition as regards the nitrogen content was practically the same. The analysis of the meat at the time of preparation showed 3.62 per cent. nitrogen and after a period of six months showed 3.69 per cent. nitrogen, or on a moisture-free basis when prepared 4.88 per cent.; and after six months 4.86 per cent. of nitrogen (see Table VI, p. 253).

Cracker Dust.—Cracker dust was purchased already ground from the manufacturer. This was thoroughly mixed, sampled, analyzed, and kept in air-tight jars.

Lard.—Pure leaf lard was used.

Bone Ash.—A good quality of finely ground bone ash was used.

Water.—Ordinary distilled water was used, such as is supplied to the chemical laboratory.

Method of Collection and Preservation of Excreta, etc.—The animal was kept in an experimental cage such as described by Gies[46] and modified by Hawk.[45] This cage was provided with a wire netting bottom of about $^3/_8$ inch mesh. Below this wire bottom, upon which the animal stands, there is arranged a sliding pan, having sides which slope at an angle of about thirty degrees. An opening was provided at the lowest point through which the urine might pass into a graduated receptacle hung from the bottom. With such a cage the urine and feces could be collected separately, the urine flowing into the receiver as soon as passed, where it was preserved by means of thymol. The feces which were, in the feeding periods, hardened by means of the ingested bone ash remained on the wire netting and were picked out with a pair of forceps. The hair and

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scurf fell through the netting to the pan and were brushed off each day. At the end of each period the whole cage was carefully washed. The cage washings consisted of scurf and small quantities of soft feces which had fallen through the netting.

The urine was collected in 24-hour periods and kept in tincture-mouth glass bottles, with ground glass stoppers. The dog was not catheterized for it was found that when the animal was allowed to urinate at will the bladder was satisfactorily emptied each day, or if a portion of the dog's urine was retained this was a fairly constant quantity. An examination of Table I, page 242, shows that the urine volumes were as a rule very close to 250 cc. per day, corresponding to a daily water ingestion of 250 cc. The other factors, such as the formation of water in metabolism and loss through respiration, would seem to compensate each other. Thymol and refrigeration[47] were used as a means of preservation.

The feces were collected when passed, dried, pulverized and the hair separated, after which the feces were analyzed. Analyses were made in periods. The hair, scurf, and cage washings were also analyzed in periods and the nitrogen distributed evenly according to the number of days in the period (see Table VI, p. 253).

The dog was weighed on a platform balance which was accurate to 0.01 kilogram.

Analyses and Methods.—Total nitrogen, urea, creatine, creatinine, allantoin, and purine determinations were made upon the urine, and total nitrogen determinations upon the feces, hair and cage washings. All urine analyses were made in duplicate and upon the 24-hour sample, except for a part of the intermediate feeding period, when analyses were made on two-day composit samples and, in the case of allantoin and purine, which were determined in composit samples of from two to ten days.

The total nitrogen was determined by the Kjeldahl method, copper sulfate[48] being used in the preliminary oxidation.

The urea was determined by the Benedict-Gephart[49] modification of the Folin[50] method. While this method has recently[51] been shown to be slightly inaccurate, due to the partial decomposition of uric acid, creatine, creatinine, allantoin, and hippuric acid,. still these substances occur in such small amounts in the urine of the dog that the urea results may be accepted as a fairly accurate indication of the amount of urea present in the urine. Ammonia was determined by the method described by Folin.[52] Creatinine was also determined by the Folin[32] procedure. The creatine was hydrolyzed in the autoclave as suggested by Benedict and Meyers.[53] Allantoin and purine were determined upon the same composit sample by the method suggested by Poduschka,[54] and modified by Underhill and Kleiner.[34]

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Blank determinations were made in all cases where possible impurities in the reagents might cause an error.

EXPERIMENTAL.

Preliminary Feeding Period.

In an investigation of this character in which the nitrogen distribution is the subject under consideration it is important that there shall be a preliminary period. During this time the subject will live under the same conditions as those which will exist during the experiment proper, and will receive a constant diet. In our case, in addition to obtaining uniform conditions of living and diet, this period served to put the animal in a condition of nitrogen equilibrium, and also to furnish data for the nitrogen partition of the urine of the animal under these normal conditions, and thus serve as a basis of comparison for the fasting and for the intermediate feeding periods.

The preliminary feeding period in this experiment extended over fifteen days. At the end of this time, during which the animal had received a uniform diet and constant water ingestion, a uniform body weight had been secured and the dog was in nitrogen equilibrium. At this point, the nitrogen balance showed an average of —0.271 gram of nitrogen per day for the eight days immediately preceding the fast. The nitrogen partition in the urine was determined for this period. The diet consisted of 70 grams of meat, 15 grams of cracker dust, 8 grams of lard, 3 grams of bone ash, and 250 cc. of water. See Table VI, p. 253. These ingredients were thoroughly mixed together and fed in the form of a broth. This diet contained 2.732 grams of nitrogen, or about 0.8 gram per kilogram body weight.

The data of the preliminary period are found in Tables I and IV, pp. 242 and 248. From a consideration of the average data for this period it will be seen that with an ingestion of 2.732 grams of nitrogen per day the dog excreted 2.762 grams of nitrogen in the urine, and suffered a further loss of 0.235 gram of nitrogen in the form of feces, hair and cage washings. This gives a minus balance of 0.271 gram of nitrogen per day. This is an approximate nitrogen equilibrium (see Table IV, p. 248).

First Fast.

At the end of the preliminary period the dog was in a fair nitrogen equilibrium, and had maintained a constant body weight for three days. The last food was given at 2 P.M., Feb. 4th, and the fast was considered as beginning at 2 P.M., Feb. 5th, the urine collected at 2 P.M. on Feb. 6th being considered as representing the urine of the first day of fast. On the first day the water (250 cc.) was placed in the food pan, but only 50 cc. were taken. As a result the urine volume for the first day was only 35 cc. and this was combined with the urine of the following day. When

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the dog refused water on the second day of fast, the fluid was given by means of a tube and this was continued throughout the fasts. On the seventh day the first feces were passed, which were very small in amount and of a pasty consistency. On the eleventh day the second fasting feces were passed; these feces were removed from the cage immediately after defecation and were greenish-brown in color, becoming black upon exposure to air. It seems probable that the fresh fasting feces of the dog are of a greenish-brown cast and only assume the black color ordinarily ascribed to them[55] upon coming in contact with the air. More fasting feces were passed on the thirteenth day of fast. The dog continued weaker and could hardly stand. Feces were again passed on the fourteenth day, but in small amount.

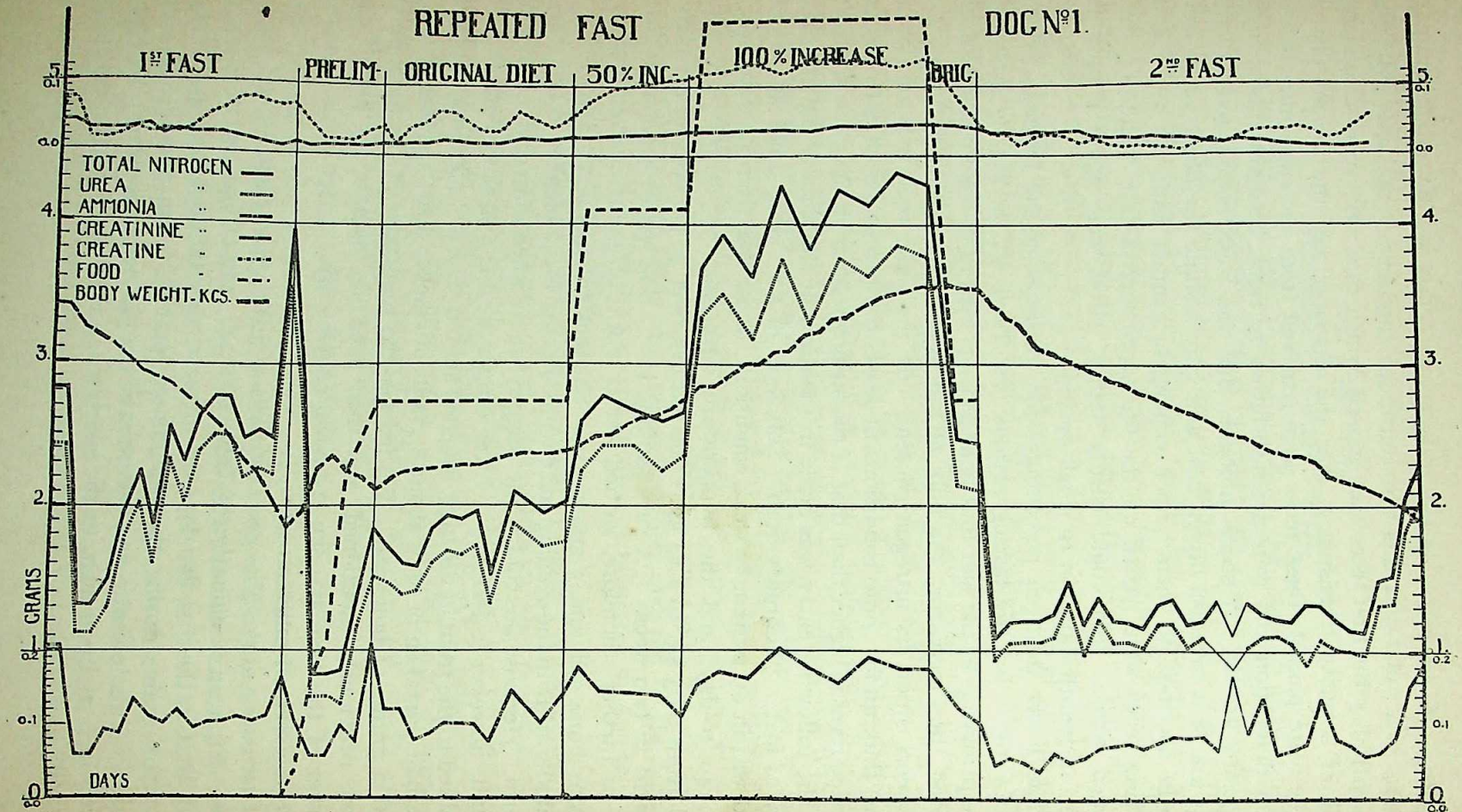
The lower nitrogen percentages for the feces of the feeding periods above those for the fasting periods (see Table VI, p. 253) is probably due primarily to the fact that bone ash was used in the diet of the feeding period thus increasing the bulk of the fecal output although having no influence upon its nitrogen content. At the same time it is no doubt true that under some conditions at least, the percentage of nitrogen in fasting feces is higher than that of the feeding feces from the same animal.[1]

The following entry was made in the diary at the close of the fifteenth day of fast. "February 20th. Soft feces in A.M. Dog could not stand and was in an extremely weak condition. Pulse rose from 54, yesterday, to 140 to-day, and the temperature sank from 37° to 36°. Weight fell from 2.05 kg. to 1.85 kg. She has lost over 40 per cent. of her body weight in two weeks. A very striking loss. Dog was so weak we feared to go further, therefore, we fed her (4 P.M.) 15 grams cracker dust, 2 grams bone ash, and 3 grams lard. She took one-half of it. Gave her remainder of it in the evening and covered her up with a blanket to keep her warm. Her nose was cold. She wagged her tail when addressed, could not stand, however (6.10 P.M.). After dinner the dog rose as we entered and walked to the front of the cage, wagging her tail. She was a new dog, and yet she had partaken of only about 8 grams of cracker dust, 3 grams of lard, and 2 grams of bone ash. We fed her the remainder of the amount of food, previously mentioned, and then fixed her blanket for her in the corner of the cage and she lay down contentedly. Later in the evening the dog seemed much stronger."

Discussion of the Nitrogen Distribution for the First Fast. Total Nitrogen.—From an examination of Table I, p. 242, and of figure on p. 224, it is seen that in the first two days the nitrogen excretion fell from an average of 2.768 grams during the preliminary period, to an average of 1.317 grams. This low nitrogen excretion is due, as has been proven by Benedict[41] in fasts upon men, to the sparing action of glycogen present in the

[1] Unpublished results from this laboratory.

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body. After the second day the nitrogen excretion in the urine rose rapidly from day to day, taking a slight drop during the twelfth to fourteenth days, and followed by a pronounced premortal rise, the nitrogen output increasing from 2.472 grams on the fourteenth day to 3.944 grams on the fifteenth day.

The rapidly increasing output of nitrogen mentioned above as occurring during the first twelve days of the fast is somewhat unusual. It might be inferred from such data, according to the commonly accepted theories with regard to the nitrogen excretion in the urine of a fasting dog, that the animal was thin and muscular, without any fat stores of any amount. Or, on the other hand, it might be argued that the dog was organically unsound. We believe both premises to be unfounded and have discussed the matter more at length on p. 234.

Urea.—The excretion of nitrogen as urea followed the total nitrogen excretion, increasing absolutely, but not relatively. The percentage urea nitrogen as compared with the total nitrogen was practically constant throughout the fast, the average being 89.13 per cent. (see Table III, p. 248) and the range being 86.36 per cent. on the sixth day to 91.12 per cent. on the seventh day (see Table II, p. 246). This average excretion is slightly higher than that found in the normal feeding period (86.79 per cent.).

This constant relation between urea and total nitrogen is contrary to the statements in the literature, [33, 34, 35] to the effect that the percentage of nitrogen as urea nitrogen decreases as the fast progresses. This fact holds for men[23, 41, 43] but it does not seem to hold for the dog, as is shown in the experiments reported from our laboratory by Howe, Mattill and Hawk. In their results the variations did not tend in any marked direction away from a constant relative value.

The fact that the method of determining the urea-nitrogen is not absolutely accurate might appear to invalidate our deductions. However, if the method determined all of the nitrogen appearing as creatine, creatinine, etc., the percentage of nitrogen as urea would not be reduced more than 3 to 4 per cent. and this would be a fairly constant quantity throughout the experiment. Therefore, this error does not detract from the accuracy of our conclusions.

Ammonia.—The ammonia-nitrogen fell from the average excretion per day of 0.143 gram of nitrogen during the feeding period to an average of 0.103 gram per day during the fast. After the first four days the ammonia excretion remained almost constant, rising slightly at the end, with the premortal rise. The relative excretion increased, then fell, and finally increased again to the end. The range in the percentage of ammonia nitrogen as compared to total nitrogen was from 3.64 per cent. on the ninth day, to 6.24 per cent. on the third day, the average per cent.

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of total nitrogen appearing as ammonia nitrogen being 4.59 per cent. (see Table II, p. 246, and Table III, p. 248).

Creatinine.—The creatinine decreased in absolute amount very gradually with but slight variations from day to day. The average daily excretion for the fast (0.025 gram of nitrogen) was below that of the feeding period (0.041 gram of nitrogen). This pronounced drop took place during the first part of the fast and from then on the absolute amount of creatinine excreted per day fell gradually, following in general the decreasing body weight. While the absolute amount of creatinine nitrogen fell very gradually, the percentage output decreased much more rapidly. The percentage of total nitrogen appearing as creatinine was 2.28 per cent. for the first two days, and then fell very regularly, as the fast progressed, to 0.46 per cent. on the last day. The grand average was 1.14 per cent. as against an average of 1.49 per cent. for the normal feeding period (see Table II, p. 246, and Table III, p. 248).

Creatine.—The creatine nitrogen fell from the feeding level (daily average of 0.056 gram of nitrogen) to an average of 0.018 gram for the first two days, and then remained approximately equal to the amount of creatinine nitrogen excreted, being in general somewhat below this value. On the ninth day the amount of creatine nitrogen excreted rose very suddenly from 0.037 gram to 0.054 gram, and continued on this higher plane, with a tendency toward an increasing excretion, to the end of the fast. The average excretion for these two portions of the fast were 0.025 gram of nitrogen for the first eight days and 0.068 gram of nitrogen for the last seven days, with a grand average of 0.046 gram of nitrogen.

The percentage of total nitrogen as creatine nitrogen increased from 1.40 per cent. on the first day to 3.10 per cent. on the twelfth day, due to the greatly increased nitrogen excretion. The average percentage of total nitrogen was 1.94 per cent. against 2.01 per cent. for the feeding period (see Table II, p. 246, and Table III, p. 248).

Allantoin and Purine.[1]—The allantoin and purine nitrogen varied from day to day. The average purine nitrogen excretion was below that of the feeding period, being 0.005 gram per day, for eleven days of the fast, against 0.012 gram of nitrogen during the feeding period. The same average amount of allantoin nitrogen as of purine nitrogen was excreted, *i. e.*, 0.005 gram while there was 0.008 gram of allantion nitrogen excreted per day, during the feeding period.

The relative amounts of nitrogen excreted as purine and allantoin nitrogen were 0.22 per cent. of purine, and 0.26 per cent. of allantoin nitrogen, while the feeding period gave 0.45 per cent. purine, and 0.31 per cent. allantoin nitrogen (see Table II, p. 246, and Table III, p. 248).

[1] These determinations were made by Mr. S. R. Wreath.

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Undetermined Nitrogen.—The undetermined nitrogen fell as a result of the fast, being 0.067 gram for an average during the fast, against 0.109 gram for the feeding period.

Intermediate Feeding Period.

General Considerations.—The object of this feeding period was to restore the animal to its original condition as regards body weight and nitrogen equilibrium. The data upon the income and outgo of nitrogen are found in Tables I and IV, pp. 242 and 248. During the portion of the feeding period immediately following the end of the first fast the diet was varied. The same constituents were fed, but the animal did not receive the full diet given in the preliminary period. The diet for the first three days did not contain any meat, and there was a minus balance of 3 grams for this period. A positive balance of 1.218 grams occurred on the fourth day, when meat was fed for the first time. During this preliminary period of four days on an extremely low diet, the animal gained 21.08 per cent. in body weight. The original diet was then fed, and continued for fifteen days, during which period the body weight increased but 7.57 per cent. In fact, during the last three days of this period there was practically no increase in weight.

It appeared that to restore the original body weight, on the normal diet, would require a very long time,[1] hence the diet was increased 50 per cent. thus causing the dog to ingest 4.104 grams of nitrogen per day. Upon this diet the dog gained 20 per cent. of its weight in eight days. The diet was again increased 50 per cent. at the end of the eight-day period of increased feeding. The animal was now receiving twice as much nitrogen per day (5.464 grams of nitrogen) as was required to maintain her constant body weight at the beginning of the experiment. Throughout these periods of increased diet (50 per cent. and 100 per cent.) the animal showed a plus nitrogen balance. After seventeen days of the 100 per cent. increase the dog had more than regained the weight lost during fasting, the weight being 3.59 kilograms, against a weight of 3.41 kilograms at the beginning of the fast. The diet was now reduced to the normal (2.732 grams of nitrogen per day). The weight dropped slightly on the first day, and remained constant for the following two days at 3.54 kilograms and at the same time the dog was in nitrogen equilibrium, there being a plus balance of 0.02 gram of nitrogen per day.

[1] That it was possible to restore the normal body weight of fasting rabbits which were fed the original diet following the breaking of the fast, has been shown by Kagan.[6] However, in these tests the animals were not brought into a condition of nitrogen equilibrium before being fasted, and the original diet may therefore have been an excessive one, thus enabling Kagan to restore the normal weight of his rabbits with greater facility than otherwise.

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In spite of the fact that the dog was giving a minus balance during the first three days of the feeding period she gained 280 grams in weight. This may have been due to the retention of water, for although the dog had been receiving 250 cc. of water daily throughout the fast, upon feeding the urine volumes for the first two days decreased to 215 and 50 cc. respectively. While the method of collecting the urine (without catheterization) does not give absolute values for the urine volumes, the values indicate that there must have been a marked water retention upon the ingestion of food. This has been previously noted in feeding after absolute fasts in dogs,[9] and also with men,[23] who had been receiving water during the fast.

Nitrogen Distribution.—The average relative amount of urea nitrogen excreted increased, as would be expected, with the increase in the diet, and the amount of nitrogen excreted per day. The percentage nitrogen output as urea dropped to the level of the preliminary period upon the resumption of the normal diet. For further discussion see p. 235.

The absolute amount of ammonia nitrogen increased with the increase in the diet. The relative amount of ammonia decreased, however, and was equal to the normal upon return to the original diet.

The creatinine nitrogen increased from day to day corresponding to the increase in muscular tissue. The average amount of creatinine excreted upon return to the original condition and body weight at the end of the intermediate feeding period was practically equal to that excreted under the normal conditions in force at the end of the preliminary feeding period, being 0.040 gram of nitrogen per day, against 0.041 gram. Relatively, however, the creatinine excretion decreased with the increase in diet and the amount of total nitrogen excreted. On the same diet (normal) the creatinine nitrogen excretion was 1.49 per cent. of the total nitrogen, during the preliminary feeding period, whereas, at the end of the intermediate feeding period, the value was 1.63 per cent. In each case the dog was in nitrogen equilibrium and of practically the same body weight.

The amount of creatine nitrogen excreted increased with the increase in the quantity of meat fed.[71] In other words the creatine ingested with the food was in part excreted in the urine.

Allantoin and purine nitrogen were both excreted in larger amounts during the fasting period. The average purine nitrogen excretion was less (0.008 gram) than that in the preliminary feeding period (0.012 gram), whereas the allantoin nitrogen was the same, *i. e.*, 0.008 gram.

Second Fast.

At the end of the feeding period, the weight of the animal was constant, within 20 grams, for a period of six days. At the beginning of the second fast the body weight was constant, although a little higher (3.54 kilograms)

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than at the beginning of the first fast (3.41 kilograms). The nitrogen balance was +0.02 gram on the day preceding the fast. The animal appeared to be in a much better physical condition than when brought to nitrogen equilibrium at the beginning of the first fast. The coat was much smoother and the muscles were very firm. The activity and attentiveness were fully as pronounced as at the beginning of the first fast.

The last food was given at 2 P.M. on April 7th and the urine collected on April 9th was taken as the first fasting urine. In this fast the water (250 cc. per day) was given entirely by means of a tube. Signs of marked weakness did not appear until about the fourteenth fasting day, and even then the dog was quite active. From then on she became gradually weaker, becoming more quiet and less disposed to move about. She became perceptibly weaker on the twenty-ninth day and at 6.15 A.M. on the thirtieth day of the fast (16 hours after the beginning of that day) the dog was found lying upon her side in a state of coma. Particulars with regard to the post-mortem examination and the histological characteristics of the tissues will be published in a later article.

Total Nitrogen.—The analytical data for the second fast are contained in Table I, p. 244, and the data are represented graphically in figure on p. 224. From an excretion of 2.435 grams on the last day of the feeding period, the total nitrogen excretion dropped on the first day of fast to 1.081 grams. This was the smallest twenty-four-hour output of nitrogen excreted at any time during the progress of the fast. The nitrogen excretion remained fairly constant for the first twenty-six days. The maximum for this time was 1.471 grams on the sixth day (when no water was given) with an average of 1.231 grams. From the twenty-sixth day on there was an increased nitrogen excretion from day to day, until on the thirtieth day an output of 2.298 grams was registered for a sixteen-hour period.

Urea.—The urea nitrogen excretion followed the total nitrogen. Relative to the total nitrogen the average for the whole fast was 86.51 per cent., the extreme values being 76.56 per cent. and 90.88 per cent. (see Table II, p. 247, and Table III, p. 248). The lower value is probably the result of alkaline fermentation, for the urine was found standing on the pan of the cage, the wire gauze which served as a filter having become clogged with hair. Aside from three days, the seventeenth, nineteenth, and twenty-third days of the fast on which alkaline fermentation probably occurred, the variation was between 81.95 per cent. and 90.88 per cent. with an average of 87.46 per cent., there being no marked tendency toward either a drop or a rise in the percentage of total nitrogen as urea.

Ammonia.—The ammonia nitrogen showed a slight tendency to increase, as the fast progressed, both absolutely and relatively. However,

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after the first six days, the excretion remained fairly constant, there being but slight variations in either direction from the mean (0.083 gram of nitrogen). This mean is a little high for it includes the three days on which alkaline fermentation probably took place, and also the last two days when the ammonia excretion was high. Excluding these, the average was 0.068 gram of nitrogen. The variations noted range from 0.039 gram to 0.085 gram of ammonia nitrogen.

Creatinine.—The creatinine nitrogen fell gradually from 0.032 gram on the first day to 0.012 gram on the twenty-sixth day, with slight variations which may be attributed to the method of urine collection (without catheterization). Unfortunately through accident we were prevented from obtaining creatine and creatinine data on the urine for the last three days of fast. The excretion of nitrogen as creatinine decreased, from day to day, both absolutely and relatively. The maximum output was 2.96 per cent. on the first day, and the minimum 0.94 per cent. on the twenty-seventh day, of fast, the average being 1.85 per cent. (see Table II, p. 247, and Table III, p. 248).

Creatine.—The creatine nitrogen fell below that of the creatinine and remained fairly constant until the fifteenth day, when it became greater than the creatinine excretion, and remained above this value to the end of the fast. On the last two days on which creatine was determined, there was a tendency toward a rise in the creatine nitrogen excretion corresponding to the premortal rise. The average creatine excretion was 0.026 gram of nitrogen per day, the extremes being 0.008 gram on the fourteenth day, and 0.053 gram on the twenty-seventh day of fast. Relative to the total nitrogen the creatine nitrogen excreted was an average of 2.05 per cent. with extremes of 0.68 per cent. on the fourteenth day and 3.64 per cent. on the twenty-sixth day (see Table II, p. 247, and Table III, p. 248).

Allantoin and Purine.—The allantoin and purine nitrogen did not show any marked tendency toward a definit variation. The average excretion was 0.005 gram of purine nitrogen per day, and 0.004 gram of allantoin nitrogen per day, which represents 0.38 per cent. of the total nitrogen as purine nitrogen, and 0.31 per cent. as allantoin nitrogen, respectively (see Table III, p. 248).

Undetermined Nitrogen.—The undetermined nitrogen was low, and practically constant in amount from day to day. It is interesting to note that the average daily amount of undetermined nitrogen in the second fast was only half that excreted during the first fast.

Discussion of the Two Fasts.

Data have been presented from two fasts upon a dog, which had previously never been subjected to an experiment of this character. The first fast continued for a period of fifteen days, or until the dog was in

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a state of collapse and the premortal rise was in evidence. This fast was followed by an intermediate feeding period of forty-seven days, during which time the animal was restored to its original condition. Following this came the second fast, which continued for thirty days, or twice as long as the first fast.

Some important factors which affect the length or intensity of a fast are the race or breed, the age, the physical condition and activity, the surrounding temperature, the character of the preliminary feeding period, the general type of the nutritional and metabolic mechanism, and whether the fast is absolute or with water. Since the two fasts were to be compared, it was essential that the animal should be as nearly as possible in the same condition as regarded body weight, nitrogen equilibrium, etc., at the commencement of each fast, and, that the experimental procedure throughout the fasts should be similarly regulated. The body weight and nitrogen equilibrium were chosen as constants to be attained before the beginning of the fast, whereas the water ingested was a constant for the whole experiment.[2, 57]

In this experiment breed and age do not enter directly. While the age of the animal affects the length of fast, in this case the dog was matured and the time between the two fasts was so short (47 days) that the age could not enter in any material way. Before each fast the dog was brought to a constant body weight, and was practically in nitrogen equilibrium. The body weight was a little greater at the beginning of the second fast, being 3.54 kilograms, while at the beginning of the first fast the weight was 3.41 kilograms. Whether this increase in weight was fat or muscular tissue will be discussed later. A lower nitrogen balance was attained than before the first fast, +0.02 gram of nitrogen against —0.271 gram before the first fast (see Table IV, p. 249). The physical condition of the animal immediately before the fasts was practically the same in the two instances. However, her coat was smoother and her muscles rather firmer at the commencement of the second fast.

Under the conditions outlined above, the dog experienced two fasts. That these were profound is evidenced by the presence of the premortal rise and the collapse of the animal in each case. The first fast was fifteen days long while the second was twice as long. These are seemingly short fasts, but considering the size and age of the dog they are of average length. The greater length of the second fast is probably due to the resistance of the tissues toward breakdown, acquired as a result of the first fast. During the first fast the tissues seem to have broken down very readily, so that the body lived improvidently upon its reserves. In the second fast, however, the protein and fat needed for the maintenance of life were used sparingly, and, as a consequence, the dog fasted longer. This low rate of katabolism may have occurred in one of two

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ways: the cells, as a result of the fast and the subsequent rebuilding, became more resistant, *i. e.*, they gave up their protein constituents less readily to the blood stream, on the other hand, the amount of protein or energy required for the functioning of the active organs, may have been lessened and consequently the latter did not draw upon the reserve protein as heavily as would have occurred had they not experienced a previous siege of fasting.

That the difference in the duration of the fasts was not a result of the amount of fat stored up in the body can be shown from consideration of the nitrogen data and body weights. The calculations on this basis follow:

Weight before the first fast	3.41 kg.	
Weight after the first fast	1.85 kg.	
Percentage loss in weight	45.75 %	
Weight before second fast	3.54 kg.	
Weight after second fast	1.91 kg.	
Percentage loss in weight	46.04 %	
Weight lost during first fast		1560 gr.
Nitrogen lost during first fast, 35.65 gr.		
Equivalent of nitrogen in terms of flesh (3.25 per cent. N)		1100 gr.
Weight of fat and water lost (by difference)		460 gr.
Weight gained during feeding		1690 gr.
Nitrogen stored during feeding, 38.25 gr.		
Equivalent of nitrogen in terms of flesh (3.25 per cent. N)		1180 gr.
Weight of fat and water stored (by difference)		510 gr.
Weight lost during second fast		1630 gr.
Nitrogen lost during second fast, 41.15 gr.		
Equivalent of nitrogen in terms of flesh (3.25 per cent. N)		1260 gr.
Weight of fat and water lost (by difference)		370 gr.

When calculating all of the nitrogen lost as flesh, and the difference between that and the loss in weight as fat, we see that during the feeding period the body increased its muscular tissue by 80 grams, and its fat by 50 grams, over the condition existing at the beginning of the first fast. We can not say positively that that which has been called fat in the above calculation is entirely fat, although the approximation is probably more accurate in the case of muscular tissue. However from a consideration of these data we may conclude that the dog was apparently in the same condition at the commencement of each fast.

The increased length of the second fast was not acccompanied by a corresponding increase in the amount of muscular tissue and fat katabolized. There was an increase of about 5.5 grams in the total weight of nitrogen lost, which amount was lost during the last three days of the fast. The calculations for the second fast show that only 370 grams of fat were lost, while 510 grams were deposited during the intermediate feeding period, leaving 140 grams of this deposited fat in the body at

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the end of the fast. The fact that the post-mortem examination showed that the animal was almost free from visible fat would contradict this statement, unless it were in the form of combined fat (phosphatides) as suggested by MacLean and Williams.[58]

Had the increased length of fast and the decreased muscular katabolism been influenced by more extensive fat deposits a much larger amount of fat would have been used than can be accounted for. It seems therefore that the phenomena were due to the altered rate of the anabolic and katabolic activities of the tissues and organs involved.

Albitsky[3] has shown that animals subjected to repeated fasting lose body weight less rapidly, and further that the length of time necessary to secure a definit body weight loss is greater than during the initial fast. A long series of repeated fasts conducted at short intervals without bringing the animal back to the normal condition between fasts may be accompanied by serious results, for Richet showed, for example, that dogs fasted repeatedly for five days at a time lived only six months, and rabbits fasted at six-day intervals lived even a shorter time.

Schulz[12] presents a theory for the explanation of the phenomena of decreased metabolism during interrupted feeding or repeated fasting. He suggests that as a result of the removal of the stimulation brought about by ingested food the activities of what is probably the most important organ involved in metabolism, *i. e.*, the liver, are impaired, and consequently the protein metabolism is led into abnormal paths and autointoxication may result. This phenomenon of autointoxication must be capable of being reduced upon the re-entrance of the stimulation of food. With the instigation of a new fast the condition of increased metabolism will not appear and as a result the injury resulting from the loss of the stimulation due to food will be very small, or will be entirely absent.

It is clear that such a theory takes no account of any metabolic activities other than those centered in the liver. While appreciating to the full the extremely important role played by this organ in the metabolic activities of the animal body, it nevertheless seems highly probable that other organs are involved in connection with the decreased protein katabolism of repeated fasting.

Schulz's[12] theory, which would account for the collapse or the premortal rise as due to a defective liver function, is not substantiated in the case of our dog, for it is evident that here the data would tend to show that there was a certain minimum amount of protein which must be present in the body in order that life shall exist. We believe this conclusion to be warranted from the fact that our data show that during each fast there were very similar amounts of nitrogen excreted notwithstanding one fast was twice as long as the other. For example, during

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the first fast of fifteen days the dog lost 10.45 grams of nitrogen per kilogram of body weight, whereas, during the second fast of thirty days she lost 11.60 grams of nitrogen per kilogram of body weight. In other words, at the end of each fast there was evidently a similar residual quantity of nitrogen-holding substance remaining in the body, the nitrogen of which was not available for the metabolic uses of the organism.

Total Nitrogen.—The amount of nitrogen excreted in the urine in each fast was approximately the same, *i. e.*, 34.689 grams in the first fast and 39.430 grams in the second. The greater absolute amount of nitrogen excreted during the second fast was due, partly, to the increased amount of nitrogen stored during the intermediate feeding period (80 grams of muscular tissue) and partly to the fact that the premortal rise of the first fast was incomplete. The average daily excretion was 2.313 grams of nitrogen for the first and 1.313 grams of nitrogen for the second fast.

During the first fast the total nitrogen excretion increased very rapidly from day to day, denoting a most pronounced acceleration of the disintegration of muscular tissue. After a drop for three days, a very marked premortal rise occurred on the last day (see Table I, p. 242, and figure on p. 224), resulting in an excretion of 3.944 grams of nitrogen, which was 1.472 grams of nitrogen more than on the previous day. This increase was greater than the average daily excretion for the whole period.

The rapid loss of nitrogen during the first fast might be ascribed to one of two things: first, a lack of fat in the body, or second, that the dog was organically unsound. If our calculations hold good (p. 232) there was more fat consumed during the first fast than during the second. The increased fat deposit (due to feeding) amounted to but 50 grams of fat, and was also accompanied by an increase in muscular tissue, and in body weight. It is evident that there must have been a good store of fat in the body before the first fast. This presumption was substantiated by the feel of the skin, which denoted an ample subcutaneous fat deposit. Furthermore, the complete recovery of the dog after the first fast, and the fact that this was followed by a subsequent fast of twice this length would denote an organically sound animal. The postmortem examination substantiated the above conclusion.

These are general deductions but sufficiently strong to warrant the premise that the first fast was normal and the increased excretion of nitrogen was due to a rapid normal katabolism of the muscular tissues. This is further substantiated by the fact that more fat was consumed during the first fast than in the second, notwithstanding the fact that approximately equal amounts of nitrogen were excreted.

The rate of nitrogen excretion in the second fast was in marked contrast to that of the first fast. After the first day the excretion remained

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almost constant for twenty-five days (an average of 1.238 grams) when a gradual premortal rise set in, the excretion for the last sixteen hours being 2.298 grams of nitrogen. The low constant excretion during the second fast was that observed in most fasts, and accompanies the increased length of time over which the amount of available nitrogen was metabolized, since practically the same total amount of nitrogen was excreted in each fast.

Urea.—The nitrogen excretion as urea followed the total nitrogen excretion both absolutely and relatively. The average percentage of urea nitrogen excreted was less in the second fast, 86.51 per cent., or, excluding the three days upon which alkaline fermentation seemed to have occurred, 87.46 per cent. In the case of the first fast the percentage excretion was 89.13 per cent. These values are higher than the average values for the normal diet. The fact that the ratio of urea nitrogen to total nitrogen was constant has been discussed, see p. 225. This constant ratio held for both fasts.

According to Folin's[50] theory, the relative amount of urea excreted varies with the amount of total nitrogen. This law was enunciated with regard to normal metabolism. It has been shown in our laboratory[23] that with fasting men the percentage of urea nitrogen decreases, at least for a time. Schöndorf[35] and Underhill and Kleiner[34] hold this to be true for the dog. The latter investigators report a fourteen-day fast, the data from which vary considerably, and the fluctuations in the percentage of urea nitrogen do not agree with those of the total nitrogen.

In fasting man the decrease in the percentage of urea is probably due to the fatty acids,[60] which by combining with the ammonia prevent the utilization of this ammonia in the formation of urea. The constant relative urea excretion in our experiment would tend to show that fatty acids or acid salts were probably not excreted in an increased amount during the fasting period.

There is a slight increase in the percentage of urea nitrogen excreted during the first fast, which would substantiate Folin's theory with regard to the effect of an increased nitrogen excretion. However, this point is more strikingly brought out in the case of the intermediate feeding period. An examination of Table III, p. 248, will show that the percentage of total nitrogen in the form of urea increased from 82.67 per cent. to 86.51 per cent., then to 87.40 per cent. and finally to 88.74 per cent. as the diet was progressively increased.

It appears, therefore, that in a fasting dog the relative urea excretion follows in general the laws of relative urea excretion which obtain for normal feeding, for, with an increased nitrogen excretion, as in the first fast, there was a slight increase in the relative urea-nitrogen excretion and with a low and constant total nitrogen excretion in the second fast,

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there was a lower and more constant relative urea excretion. Why this should hold for the dog and not for man is not clear. It may be, perhaps, that the dog, being a carnivorous animal, and living on the same form of food in each case (fresh lean meat, and muscular tissue), excretes in each instance the same percentage of total nitrogen in the form of urea. Man, on the other hand, being unaccustomed to a diet of uncooked lean meat, finds the conditions unusual when forced to exist upon his own tissues during a fasting test, and consequently under these conditions a different quota of the total nitrogen output is eliminated as urea than when he ingests the normal mixed diet.

Ammonia.— The ammonia-nitrogen excretion was less for the daily average in the second fast, 0.083 gram or, excluding the questionable days already mentioned, 0.068 gram of nitrogen per day, as against 0.103 gram of nitrogen in the first fast. Instead of increasing from day to day, as in the fasts of men, the ammonia remained fairly constant, following the total nitrogen excretion, as Folin[56] has pointed out, only in that when the total nitrogen excretion was low, the ammonia was absolutely lower, but relatively higher. A rise in the ammonia excretion at the end corresponded in each case with the premortal rise. The average ratio of ammonia nitrogen to total nitrogen was in the first fast 4.59 per cent., and in the second fast 6.12 per cent., or, excluding the days of alkaline fermentation, 5.66 per cent., which shows the relatively higher ammonia excretion during the second fast. The facts noted here with regard to the ammonia excretion are those which hold in normal feeding.

Creatinine.—The marked differences in the total nitrogen excretions were not accompanied by similar changes in the creatinine-nitrogen output. In both fasts the creatinine nitrogen fell gradually, the average daily excretion for each period being almost the same, that for the first fast being 0.025 gram of nitrogen and for the second 0.023 gram. The total amount excreted in the second fast was nearly twice as great as that of the first fast, the output of creatinine nitrogen, therefore, varying inversely as the length of the fast.

Folin[56] first enunciated the law that the amount of creatinine excreted in the urine by a normal individual is quite independent of either the amount of protein in the food, or the total nitrogen in the urine. This has been confirmed by van Hoogenhuyze and Verploegh,[40] Klerker,[61] Closson[62] and Shaffer,[63] whereas Cathcart[64] and Paton[65] fail to verify this theory. Folin has further pointed out that the chief factor determining the amount of creatinine eliminated appears to be the weight of the individual, and that it also depends upon the mass of active protoplasmic tissue. Shaffer[63] virtually substantiates this theory. The creatinine elimination in fasting man has been observed by van Hoogenhuyze and Verploegh, Benedict,[41] Benedict and Diefendorf[42] and Cathcart,[66] and in the fasting

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dog by Underhill and Kleiner,[34] and Howe, Mattill and Hawk,[23] a gradual decrease having been observed in each case. Underhill and Kleiner state that the creatinine excretion is variable. Shaffer lays stress upon the creatinine coefficient (milligrams per kilogram body weight) as a constant for individuals of an equal muscular efficiency, which should then decrease for a decreasing muscular efficiency.

The data from our experiment confirm, in the main, these theories. With a decreasing body weight (loss of muscular tissue) and muscular efficiency there is a decrease in the amount of creatinin excreted and also in the creatinine coefficient (Table V, p. 250). The quantity of creatinine excreted, per day, bears a direct relation to the mass of active muscular tissue present in the body. The creatinine excreted in our experiment does not bear any direct relation to the nitrogen excretion, for we have a similar excretion of creatinine in the two fasts, notwithstanding the fact that the rate of the nitrogen excretion was markedly different in the two cases and that the average daily excretion of total nitrogen was nearly 100 per cent. greater in the first than in the second fast.

That it is the decrease in the amount of active protoplasm, and not merely in the body weight, which causes a decrease in the creatinine excretion may be seen from an examination of the data relative to the creatinine coefficient. If the decrease were coincident with the decrease in weight the creatinine coefficient would remain constant, whereas in reality it decreases more slowly than the body weight. This dependence upon the mass of muscular tissue is shown in the intermediate feeding period. As the dog gained in weight and stored nitrogen the quantity of creatinine increased, although it did not bear any direct relation to the amount of nitrogen excreted. On the nineteenth day, or at the time 34 per cent. of the body weight lost in the fast, and one-fourth the nitrogen lost had been restored, the creatinine coefficient was nearly equal to that before the fast. Furthermore, on the twenty-fifth day or at the time the animal had regained 50 per cent. of its lost nitrogen and body weight, *the creatinine coefficient was the same* as that secured before the fast when the dog was of constant body weight and in nitrogen equilibrium. If current ideas regarding this coefficient are correct the findings indicate that the animal possessed equal muscular efficiency under the two conditions.

The above may be substantiated by the following data:

Total amount of nitrogen lost during first fast..... 34.689 g.
Creatinine coefficient before fast = 12 mg.
Nitrogen stored during 19 days of feeding (creatinine coefficient 11 mg.)
and 34 per cent. gain in body weight..... 9.015 g.
Nitrogen stored during 25 days of feeding (creatinine coefficient 12 mg.)
and 50 per cent. in body weight..... 17.157 g.

We thus see that by the time the original creatinine coefficient was restored, *i. e.*, on the twenty-fifth day of feeding, the mass of muscle was

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only 50 per cent. of that present before the fast. If we are to hold to the idea that the ingested creatine (in the meat) and the amount of nitrogen excreted have no effect upon the creatinine output, then in order that the creatinine coefficient shall be significant, we must suppose a return to the original condition as regards muscular efficiency when the animal had only restored one-half of its nitrogen and body weight. The dog certainly, at this point in the experiment, exhibited all of her normal activity, which fact tends to confirm the above remarks with regard to muscular efficiency.

Creatine.—The excretion of creatine in the two fasts was quite similar, being marked by a drop in the creatine-nitrogen excretion at the beginning of the fast, followed by a period during which the creatine nitrogen remained fairly constant, and a little less than the creatinine excretion. Toward the end of the fast, and before the premortal rise there was a sudden increase in the amount of creatine nitrogen excreted, being greater than the creatinine excretion. This increased creatine continued to the end. This marked increase of the creatine excretion over the amount of creatinine excreted seems to be an indication of the pronounced metabolic irregularities which finally result in the inception of the premortal rise, and occurs from two to three days before the drop in the total nitrogen excretion, which precedes this rise.

The amount of creatine excreted in the two fasts is almost equal, corresponding to the amount of total nitrogen excreted during the periods in which creatine was determined. Benedict,[67] Mellanby,[68] Shaffer,[63] Paton,[65] Fowler and Hawk[57] and others have furnished experimental evidence in support of the theory that the creatine in the urine arises as a result of the breakdown of the muscular tissues. Paton suggested that the discrepancy between the amount of flesh which was katabolized as calculated from the creatine output and that calculated from the total nitrogen may be due to the resynthesis of a part of the nitrogen of the broken-down muscular tissue, the creatine being excreted at the time of the muscle breakdown.

Calculating upon the basis of the excretions of total nitrogen and creatine nitrogen we have derived in each case the weight of the mass of tissue katabolized, assuming the accuracy of the theory that urinary creatine represents disintegrated muscular tissue. The data are appended:

FLESH LOST AS CALCULATED FROM THE URINARY TOTAL NITROGEN DATA AND FROM THE CREATINE NITROGEN DATA.

First Fast (15 days).

Nitrogen lost—34.689 grams.

Equivalent in terms of flesh—(3.25%) = 1069 grams

Creatine nitrogen lost—0.684 gram

Equivalent in terms of flesh (0.123%) = 555 grams

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Second Fast (27 days).
Nitrogen lost—33.524 grams
Equivalent in terms of flesh (3.25%) = 1030 grams
Creatine nitrogen lost—0.689 gram
Equivalent in terms of flesh—(0.123%) = 560 grams

The amount of creatine nitrogen present in the muscles of the dog at the end of the fast was 0.042 per cent.,[70] showing a very marked decrease (66 per cent.) in the amount of creatine in the fasting muscle remaining in the body. Dorner has reported a somewhat smaller decrease in the case of rabbits' muscle. His data show the amount of creatine in this tissue to be reduced from 0.456 per cent. to 0.356 per cent. as a result of fasting. This pronounced decrease of creatine found by us in fasting muscle is a most significant fact and shows clearly that in fasting we cannot with accuracy consider the total amount of excreted creatine as resulting from the complete and permanent disintegration of muscular tissue. However, even if we do consider all of the excreted creatine as having this origin we have shown by calculation that we can account for only about one-half of the total nitrogen on this basis. The discrepancy between the mass of muscular tissue lost, calculated on the two bases, *i. e.*, total nitrogen and creatine nitrogen output becomes all the more striking when we appreciate that a large part of the creatine excreted during the fasts and which is ordinarily considered as representing completely disintegrated muscular tissue, in reality most certainly does not represent this but rather has been withdrawn from muscular tissue which is still functioning as living tissue within the body of the animal. Unfortunately no determination was made of the actual mass of muscular tissue remaining in the body after fasting. However, inasmuch as we have shown in this laboratory[70] that the total nitrogen content of fasting muscle is only slightly lower than that of well-nourished muscle it is evident that but a small fraction of the total nitrogen excreted by the urine arose from the muscular tissue still functioning within the body, whereas a comparatively large part of the creatine had this origin. When all these facts are taken into consideration it is apparent that over 50 per cent. of the total nitrogen of the urine had a source other than the katabolism of muscular tissue. The fact that fasting muscle may have its creatine store depleted to one-third the normal while retaining its nitrogen content but slightly lowered indicates rather conclusively that the creatine is held in such a combination within the muscle that its release is not necessarily accompanied by the disintegration of the other nitrogenous muscle constituents, which go to form the total nitrogen of muscular tissue.[68, 57] At the same time we must not lose sight of the fact that the muscular tissue whose nitrogen store is seemingly intact at the end of a fast may assume this condition not because the katabolic processes

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have not been sufficiently profound to alter its inner structure but rather because of certain synthetic reactions which have followed or accompanied the primary disintegration of the tissues.[65] That there is a direct relation between the amount of nitrogenous material katabolized and the creatine excreted is brought out in our results. For example, with practically the same amount of nitrogen excreted under the same conditions, *i. e.*, two fasts continuing to the premortal rise, and with two equal but decidedly different rates of nitrogen excretion, practically the same amount of creatine was excreted.

No direct evidence has been obtained which would show the relation between creatine and creatinine. The creatine appears to be derived either from disintegrating muscular tissue or to be removed in some manner from such tissues which are still functioning within the body. The creatine excretion was low during the first part of each fast, increasing suddenly a few days before the drop in the total nitrogen excretion which preceded the premortal rise. From this time to the end of the fast the daily output of creatine nitrogen exceeded that of the creatinine nitrogen. Dorner,[69] in the case of a rabbit which died after nine days of fasting, found the creatine excretion of the second day to exceed that of creatinine.

Summary.

A fox terrier bitch about one year old and weighing 3.41 kilograms was brought into nitrogen equilibrium and was subjected to two fasts. On the fifteenth day of the first fast the premortal rise in nitrogen output was noted and was accompanied by other signs indicating that death would result in a few hours. She was then carefully fed and during the feeding period of forty-seven days regained her former weight and was again brought into nitrogen equilibrium, after which she was fasted a second time for a period of thirty days. The animal was in fully as good physical condition at the beginning of the second as she was at the commencement of the first fast.

The water ingestion was uniform (250 cc.) throughout the feeding and fasting periods. The loss in body weight was nearly equal in each fast, being 45.75 per cent. for the first and 46.04 per cent. for the second fast. However, on the fifteenth day of the second fast, *i. e.*, after a period equaling in length the entire first fast, the animal had lost but 25.42 per cent. of her body weight.

From the data obtained we have shown that:

1. With a practically equal total nitrogen excretion, the rate of this excretion was widely different in the two fasts, being high and rapidly increasing during the first fast of fifteen days, and low and fairly constant during the second fast of thirty days. A premortal rise occurred at the end of each fast.

2. The absolute amount of urea nitrogen excreted was in direct rela-

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tion to the total nitrogen excretion. The relative urea-nitrogen excretion remained practically constant throughout the fasts, but increased with an increased total nitrogen excretion during the intermediate feeding period.

3. The ammonia-nitrogen excretion remained fairly constant, varying with the total nitrogen excretion in that when this was low the ammonia-nitrogen was absolutely lower but relatively higher.

4. The creatinine-nitrogen excretion decreased very uniformly and gradually as the fasts progressed, and increased uniformly and gradually during the intermediate feeding period. The total output of creatinine nitrogen varied inversely as the length of the fast. On the nineteenth day of the feeding period, or at the time thirty-four per cent. of the body weight lost in the first fast, and one-fourth the nitrogen lost, had been restored, the creatinine coefficient was nearly equal to that before the fast. Furthermore, on the twenty-fifth day or at the time the animal had regained only fifty per cent. of its lost nitrogen and body weight, the creatinine coefficient was *the same* as that secured before the fast when the dog was of constant body weight and in nitrogen equilibrium.

5. The total amount of creatine nitrogen excreted was practically the same during each fast. The average daily amount of creatine nitrogen, however, was nearly twice as great during the first fast as during the second fast.

6. The allantoin and purine nitrogen excretions decreased as a result of the fast and were practically equal for each fast.

7. The undetermined nitrogen decreased as a result of fasting. The average daily amount of undetermined nitrogen in the second was one-half that in the first fast.

8. A consideration of the summation of the nitrogen balances shows that there is a minimum amount of nitrogen which must be present in the body in order that life shall exist.

9. The excretion of urinary creatine increased suddenly a few days before the drop in the total nitrogen excretion which precedes the premortal rise. From this time to the end of the fast the daily output of creatine nitrogen exceeded that of the creatinine nitrogen.

10. Assuming the accuracy of the theory that the urinary creatine represents disintegrated muscular tissue and calculating accordingly, a discrepancy exists between the calculated mass of muscular tissue lost, when considered from the standpoint of total nitrogen and creatine nitrogen respectively. When all the facts in this connection are taken into consideration it is apparent that over fifty per cent. of the total nitrogen had a source other than the muscular tissue.

11. The creatine content of muscle showed a marked decrease (over sixty per cent.) as a result of fasting, while the nitrogen content of similar

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TABLE I.—GENERAL DATA.

Day of Expt.	Body weight. Kgs.	Volume of urine. cc.	Specific gravity.	Reaction of urine.	Total N. Grams.	Urea N. Grams.	Ammonia N. Gram.	Creatinine N. Gram.	Creatine N. Gram.	Purine N. Gram.	Allantoin N. Gram.	Undeter. N. Gram.
					Preliminary Feeding Period.							
1	3.50	270	10125	?	2.707	2.354	0.104	0.051	0.008	...	...	0.190
2	..	256	1013	acid	2.202	1.940	0.092	0.037	0.079	...	0.002	0.032
3	..	270	10145	acid	2.630	2.279	0.122	0.040	0.033	...	0.003	0.153
4	3.46	265	1012	acid	2.580	2.240	0.118	0.038	0.052	0.015	0.004	0.113
5	..	260	1013	alk.	2.555	2.168	0.145	0.036	0.013	0.006	0.023	0.164
6	3.42	240	1014	alk.	2.964	2.524	0.205	0.043	0.074	0.016	0.010	0.092
7	3.40	310	1014	acid	3.683	3.312	0.156	0.040	0.121	...	0.009	0.046
8	3.41	245	10105	acid	2.825	2.425	0.206	0.041	0.074	...	...	0.079
					First Fast.							
1	3.26	262	10115	acid	2.634	2.305	0.118	0.060	0.037	0.006	0.013	0.095
2	3.19											
3	3.13	235	10055	acid	1.489	1.293	0.093	0.029	0.021	...	...	0.053
4	3.04	188	1011	acid	1.960	1.755	0.087	0.032	0.032	...	...	0.054
5	2.95	219	10125	acid	2.250	2.020	0.132	0.036	0.023	0.012	0.008	0.029
6	2.91	255	10065	acid	1.862	1.608	0.113	0.023	0.030			0.076
7	2.86	164	1014	acid	2.558	2.331	0.102	0.029	0.026	...	...	0.070
8	2.77	288	10075	acid	2.308	2.037	0.118	0.026	0.037	0.001	0.001	0.088
9	2.68	260	1010	acid	2.637	2.399	0.096	0.026	0.054	0.006	...	0.056
10	2.60	267	10095	acid	2.780	2.502	0.102	0.026	0.062	0.006	0.002	0.080
11	2.49	262	10095	acid	2.777	2.495	0.105	0.024	0.075	0.012	0.004	0.062
12	2.31	292	10085	acid	2.483	2.208	0.109	0.019	0.077	0.001	0.002	0.067
13	2.22	280	1009	acid	2.535	2.261	0.105	0.015	0.071	0.004	0.004	0.075
14	2.05	283	1009	acid	2.472	2.214	0.110	0.012	0.069	0.007	0.007	0.053
15	1.85	325	1013	acid	3.944	3.544	0.160	0.016	0.070	...	0.012	0.142

					Feeding Periods.							
					Preliminary.							
1	1.95	215	1011	acid	2.893	2.633	0.104	0.010	0.044	...	...	0.116
2	2.25	311	10145	acid	1.670	1.377	0.117	0.025	0.050	0.007	0.008	0.086
3	2.35											
4	2.24	443	1006	acid	0.860	0.641	0.095	0.014	0.022	0.004	0.008	0.076
					Normal Diet.							
5	2.20	250	1008	alk.	1.356	1.160	0.079	0.013	0.036			0.061
6	2.12	258	1008	alk.	1.840	1.496	0.211	0.017	0.043			0.066
7	2.19	241	10075	alk.	1.716	1.465	0.119	0.016	0.015	0.029	0.004	0.094
8	2.24	250	1008	acid	1.595	1.381	0.101	0.018	0.041			0.047
9	2.25	238	1007	alk.	1.575	1.406	0.078	0.018	0.048			0.018
10	2.26	257	1008	alk.	1.835	1.599	0.087	0.021	0.065			0.057
11	2.27	269	1009	alk.	1.929	1.678	0.101	0.020	0.061			0.063
12	2.29	250	1009	alk.	1.900	1.659	0.100	0.018	0.047	0.024		0.070
13	2.28	258	10085	alk.	1.952	1.717	0.100	0.027	0.071			0.075
14	2.31	198	1010	alk.	1.515	1.319	0.077					0.051
15	2.34	100	1011	alk.	4.368	3.740	0.289	0.048	0.127	0.018	0.029	0.133
16	2.36	385	1011	amph.								
17	2.36	235	1010	acid	3.889	3.433	0.204	0.044	0.082			0.088
18	2.36	265	10105	amph.								
19	2.38	240	1009	amph.	2.030	1.750	0.140	0.026	0.058	0.028	0.050	0.037
					50% Increase in Diet.							
20	2.42	212	1013	amph.	2.594	2.236	0.179	0.026	0.079			0.055
21	2.49	235	10125	amph.	5.545	4.837	0.288	0.052	0.191			0.135
22	2.50	295	10125	acid						0.026	0.075	
23	2.57	250	1013	acid	5.535	4.848	0.283	0.056	0.203			0.094
24	2.61	265	1013	acid								
25	2.63	248	10125	acid	5.183	4.547	0.276	0.061	0.219	0.014	0.023	0.040
26	2.67	225	1014	acid								
27	2.75	232	1012	acid	2.655	2.343	0.110	0.035	0.120	0.009	0.006	0.032

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TABLE I (*continued*).

Day of expt.	Body weight. Kgs.	Volume of urine. cc.	Specific gravity.	Reaction of urine.	Total N. Grams.	Urea N. Grams.	Ammonia N. Gram.	Creatinine N. Gram.	Creatine N. Gram.	Purine N. Gram.	Allantoin N. Gram.	Undeter. N. Gram.
						100% Increase in Diet.						
28	2.84	267	1017	acid	3.682	3.250	0.152	0.035	0.120	0.009	0.006	0.110
29	2.85	304	10145	amph.	7.858	7.010	0.344	0.068	0.246	...	0.029	0.161
30	2.92	235	10175	acid								
31	3.00	215	1017	acid	7.286	6.380	0.325	0.072	0.269	...	0.020	0.220
32	3.00	255	10175	acid								
33	3.09	250	1020	acid	8.577	7.515	0.406	0.076	0.241	...	0.015	0.324
34	3.10	275	10195	amph.								
35	3.20	220	1020	acid	7.606	6.580	0.378	0.076	0.283	0.022	0.016	0.232
36	3.24	230	1021	alk.								
37	3.32	265	1020	acid	8.560	7.533	0.357	0.086	0.290			0.254
38	3.35	258	10185	acid								
39	3.40	211	1023	amph.	8.283	7.275	0.387	0.082	0.276			0.223
40	3.46	215	10225	amph.						0.131	0.032	
41	3.50	212	1024	amph.	8.762	7.695	0.355	0.089	0.258			0.325
42	3.52	260	1019	acid								
43	3.56	220	10215	acid	8.592	7.550	0.351	0.089	0.298			0.262
44	3.59	240	1023	amph.								
						Normal Diet.						
45	3.56	200	1014	acid	4.920	4.290	0.228	0.082	0.170	0.024	0.016	0.134
46	3.54	250	1012	acid								
47	3.54	224	1013	acid	2.435	2.105	0.111	0.039	0.046			0.121
						Second Fast.						
1	3.42	230	10055	acid	1.081	0.941	0.046	0.032	0.029	...	0.006	0.030
2	3.32	252	1005	acid	1.197	1.036	0.058	0.032	0.031			0.037

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3	3.26	212	1005	acid	1.209	1.058	0.052	0.030	0.014			0.046
4	3.11	295	10075	alk.	1.202	1.059	0.039	0.034	0.028			0.033
5	3.07	216	10045	acid	1.251	1.086	0.062	0.031	0.032	0.021	0.027	0.031
6	2.94	264[1]	1023[1]	acid	1.471	1.317	0.051	0.034	0.026			0.034
7	3.05	122	10085	acid	1.128	0.985	0.057	0.027	0.018			0.032
8	2.95	248	1005	acid	1.368	1.209	0.070	0.026	0.024			0.030
9	2.89	255	1004	acid	1.218	1.063	0.074	0.025	0.016			0.029
10	2.86	214	1005	acid	1.194	1.056	0.075	0.026	0.012	0.019	0.024	0.016
11	2.80	241	10035	acid	1.158	1.026	0.070	0.024	0.014			0.015
12	2.77	204	10045	acid	1.332	1.173	0.078	0.027	0.019			0.026
13	2.72	231	1005	amph.	1.357	1.192	0.085	0.025	0.014			0.037
14	2.68	210	1005	amph.	1.182	1.028	0.083	0.024	0.008			0.035
15	2.64	209	1005	acid	1.207	1.097	0.084	0.023	0.016	...	0.017	...
16	2.58	233	1005	amph.	1.344	1.183	0.066	0.020	0.023			0.048
17	2.51	232	1004	alk.	1.119	0.879	0.167	0.018	0.018			0.033
18	2.49	197	1005	amph.	1.193	1.025	0.085	0.021	0.025			0.033
19	2.45	231	10045	amph.	1.335	1.094	0.138	0.020	0.035			0.041
20	2.40	224	1004	acid	1.257	1.107	0.062	0.018	0.036	0.026	0.010	0.027
21	2.37	215	1004	acid	1.221	1.056	0.067	0.016	0.035			0.040
22	2.36	215	1005	acid	1.203	0.921	0.076	0.014	0.038			0.148
23	2.31	260	10055	amph.	1.315	1.079	0.139	0.013	0.033			0.042
24	2.21	246	10045	acid	1.216	1.071	0.082	0.012	0.024			0.018
25	2.18	217	1004	acid	1.145	1.003	0.074	0.012	0.027	0.029	0.017	0.020
26	2.15	215	1004	acid	1.126	0.971	0.060	0.012	0.041			0.033
27	2.11	232	1005	acid	1.495	1.318	0.065	0.014	0.053			0.036
28	2.05	252	10055	acid	1.519	1.329	0.083	...	...	...	...	...
29	1.97	271	1007	acid	2.089	1.826	0.153	...	...	...	...	...
30	1.91	198	1015	alk.	2.298	2.036	0.182	...	...	...	...	...

[1] 66 cc. of urine, diluted to 264 cc.

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TABLE II.—PERCENTAGE NITROGEN DISTRIBUTION.

Day.	Urea N.	Ammonia N.	Creatinine N.	Creatine N.	Purine N.	Allantoin N.	Undeter. N.
Preliminary Feeding Period.							
1	86.96	3.84	1.88	2.95	..	..	0.70
2	88.10	4.18	1.68	3.59	..	0.09	1.45
3	86.65	4.64	1.52	1.25	..	0.11	5.82
4	86.82	4.57	1.47	2.01	0.58	0.16	4.38
5	84.85	5.67	1.41	0.51	0.24	0.90	6.42
6	85.15	6.92	1.45	2.49	0.54	0.34	3.10
7	89.93	4.24	1.08	3.28	..	0.24	1.25
8	85.84	7.29	1.45	2.62	..	..	2.79
First Fast.							
1, 2	87.51	4.48	2.28	1.40	0.23	0.49	3.60
3	86.84	6.24	1.95	1.41	..	..	3.56
4	89.54	4.44	1.63	1.63	..	..	2.75
5	89.78	5.87	1.60	1.02	0.27	0.18	1.29
6	86.36	6.07	1.23	1.61	0.32	0.21	4.08
7	91.12	3.99	1.13	1.02	..	..	2.74
8	88.26	5.11	1 13	1.60	0.04	0.04	3.81
9	90.97	3.64	0.98	2.05	0.23	..	2.12
10	90.00	3.67	0.93	2.23	0.22	0.07	2.88
11	89.84	3.78	0.86	2.70	0.43	0.14	2.23
12	88.92	4.39	0.76	3.10	0.04	0.08	2.70
13	89.19	4.14	0.59	2.80	0.16	0.16	2.96
14	89.56	4.45	0.48	2.79	0.28	0.28	2.14
15	89.86	4.06	0.46	1.77	..	0.30	3.60
Feeding Periods.							
Preliminary.							
1	91.01	3.59	0.34	1.52	..	..	4.01
2–3	82.45	7.00	1.50	2.99	0.42	0.48	5.15
4	74.53	11.05	1.63	2.56	0.46	0.93	8.84
Normal Diet.							
5	85.55	5.82	0.96	2.65	0.44	0.07	4.50
6	81.30	11.46	0.92	2.34	0.33	0.05	3.59
7	85.37	6.93	0.93	0.87	0.35	0.06	5.48
8	86.58	6.33	1.13	2.57	0.38	0.06	2.95
9	89.27	4.95	1.14	3.05	0.38	0.06	1.14
10	87.14	4.74	1.14	3.54	0.33	..	3.11
11	86.99	5.23	1.04	3.16	0.31	..	3.27
12	87.31	5.26	0.94	2.47	0.32	..	3.68
13	87.96	5.12	0.78	1.84	0.31	..	3.84
14	87.06	5.08		2.31	0.40	0.59	3.37
15–16	85.62	6.61	1.10	2.91	0.27	0.43	3.04
17–18	88.27	5.24	1.12	2.11	0.36	0.64	2.26
19	86.21	6.90	1.38	2.86	0.34	0.59	1.82
50% Increase in Diet.							
20	86.21	6.90	1.00	3.04	0.27	0.46	2.12
21–22	87.23	5.19	0.94	3.44	0.23	0.68	2.43

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TABLE II (*continued*).

Day.	Urea N.	Ammonia N.	Creatinine N.	Creatine N.	Purine N.	Allantoin N.	Undeter. N
			50% Increase in Diet.				
23–24	87.59	5.11	1.01	3.67	0.24	0.69	1.61
25–26	87.73	5.32	1.17	4.23	0.27	0.44	0.77
27	88.25	4.14	1.32	4.52	0.34	0.23	1.21
			100% Increase in Diet.				
28	88.25	4.13	0.95	3.26	0.24	0.16	2.99
29–30	89.21	4.38	0.86	3.13	..	0.37	2.05
31–32	87.56	4.46	0.99	3.69	..	0.27	3.02
33–34	87.62	4.73	0.88	2.81	..	0.17	3.78
35–36	86.51	4.97	1.00	3.72	0.28	0.21	3.05
37–38	88.02	4.17	1.00	3.39	0.37	0.05	2.97
39–40	87.83	4.67	0.99	3.33	0.39	0.05	2.69
41–42	87.82	4.05	1.01	2.94	0.36	0.05	3.71
43–44	87.87	4.08	1.03	3.47	0.37	0.05	3.05
			Normal Diet.				
45–46	87.19	4.63	1.67	3.46	0.33	0.20	2.72
47	86.44	4.56	1.60	1.89	0.33	0.21	4.97
			Second Fast.				
1	87.05	4.25	2.96	2.68	..	0.28	2.78
2	86.54	4.84	2.67	2.59	..	0.25	3.09
3	87.51	4.30	2.48	1.16	0.33	0.41	3.80
4	88.10	3.25	2.82	2.33	0.33	0.42	2.74
5	86.81	4.95	2.48	2.56	0.32	0.40	2.48
6	89.53	3.46	2.31	1.77	0.27	0.34	2.31
7	87.32	5.05	2.39	1.60	0.36	0.44	2.84
8	88.38	5.12	1.90	1.75	0.29	0.36	2.19
9	87.27	6.07	2.05	1.31	0.33	0.41	2.38
10	88.44	6.28	2.18	1.01	0.34	0.42	1.34
11	88.60	6.03	2.07	1.21	0.34	0.43	1.29
12	88.06	5.85	2.02	1.43	0.30	0.37	1.95
13	87.84	6.26	1.84	1.03	..	0.30	2.73
14	86.97	7.02	2.03	0.68	..	0.34	2.96
15	90.88	6.96	1.90	1.32	..	0.33	..
16	88.02	4.91	1.49	1.71	..	0.30	..
17	78.54	14.92	1.61	1.61	..	0.36	2.95
18	85.92	7.12	1.76	2.10	..	0.34	2.77
19	81.95	10.30	1.50	2.62	0.37	0.15	3.07
20	88.07	4.93	1.43	2.86	0.40	0.16	2.15
21	86.49	5.49	1.31	2.87	0.41	0.16	3.27
22	76.56	6.32	1.16	3.16	0.42	1.17	12.30
23	82.05	10.57	0.99	2.51	0.46	0.23	3.19
24	88.08	6.74	0.98	1.97	0.49	0.25	1.48
25	87.59	6.46	1.05	2.36	0.52	0.26	1.75
26	86.23	5.33	1.06	3.64	0.53	0.27	2.93
27	88.16	4.35	0.94	3.54	0.41	0.20	2.41
28	87.49	5.46	..	..	..	..	..
29	87.41	7.33	..	..	..	..	..
30	88.59	7.92	..	..	..	..	..

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TABLE III.—SUMMARY OF NITROGEN EXCRETION.

Period (diet).	Total N.	Urea N.	Ammonia N.	Creatinine N.	Creatine N.	Purine N.	Allantoin N.	Undet. N.
Period Averages—Grams per Day.								
Preliminary	2.768	2.405	0.143	0.041	0.056	0.012	0.008	0.109
First Fast	2.313	2.065	0.103	0.025	0.046	0.005	0.005	0.067
Prelim. Feed.	1.356	1.162	0.105	0.012	0.029			0.070
Normal	1.833	1.587	0.112	0.020	0.054			0.076
50%	2.689	2.351	0.142	0.028	0.102	0.008	0.008	0.045
100%	4.071	3.576	0.178	0.040	0.134			0.124
Normal	2.452	2.132	0.113	0.040	0.072			0.085
Second Fast	1.314	1.141	0.083	0.023	0.026	0.005	0.004	0.032
Period Averages—Per cent.								
Preliminary		86.79	5.17	1.49	2.01	0.45	0.31	4.03
First Fast		89.13	4.59	1.14	1.94	0.22	0.26	2.89
Prelim. Feed.		82.67	7.21	1.11	2.36	0.45	0.71	6.00
Normal		86.51	6.13	1.05	2.51	0.35	0.28	3.25
50%		87.40	5.33	1.09	3.78	0.27	0.50	1.63
100%		88.74	4.40	0.97	3.30	0.40	0.15	3.03
Normal		86.81	4.59	1.63	2.68	0.33	0.20	3.56
Second Fast		86.51*	6.12†	1.85	2.05	0.38	0.31	2.58
Total Weight of Nitrogen Excreted in Urine (Grams).								
First Fast	34.689	30.972	1.550	0.373	0.684	...	...	...
Second Fast	39.430	34.224	2.483	0.611	0.689	...	...	...

TABLE IV.—NITROGEN BALANCES.

Day.	N in urine. Grams.	N in hair, feces and cage wash. Gram.	Total N output. Grams.	N in food. Grams.	N balance.
Preliminary Period.					
1	2.707	0.235	2.942	2.732	— 0.210
2	2.202	0.235	2.437	2.732	+ 0.295
3	2.630	0.235	2.865	2.732	— 0.133
4	2.580	0.235	2.815	2.732	— 0.083
5	2.555	0.235	2.790	2.732	— 0.058
6	2.964	0.235	3.199	2.732	— 0.467
7	3.683	0.235	3.918	2.732	— 1.186
8	2.825	0.235	3.060	2.732	— 0.328
First Fast.					
1, 2	2.634	0.064	2.762	...	— 2.762
3	1.489	0.064	1.553	...	— 1.553
4	1.960	0.064	2.024	...	— 2.024
5	2.250	0.064	2.314	...	— 2.314
6	1.862	0.064	1.926	...	— 1.926
7	2.558	0.064	2.622	...	— 2.622
8	2.308	0.064	2.372	...	— 2.372
9	2.637	0.064	2.701	...	— 2.701
10	2.780	0.064	2.844	...	— 2.844

* See discussion, p. 229.

† See discussion, p. 229–30.

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TABLE IV (*continued*).

Day.	N in urine. Grams.	N in hair, feces and cage wash. Gram.	Total N output. Grams.	N in food. Grams.	N balance.
		First Fast.			
11	2.777	0.064	2.841	...	— 2.841
12	2.483	0.064	2.547	...	— 2.547
13	2.535	0.064	2.599	...	— 2.599
14	2.472	0.064	2.536	...	— 2.536
15	3.944	0.064	4.008	...	— 4.008
		Feeding Periods.			
		Preliminary.			
1	2.893	0.161	3.054	0.198	— 2.856
2, 3	1.670	0.161	1.992	1.848	— 0.144
4	0.860	0.161	1.021	2.239	+ 1.218
		Normal Diet.			
5	1.356	0.161	1.517	2.465	+ 0.948
6	1.840	0.161	2.001	2.732	+ 0.731
7	1.716	0.161	1.877	2.732	+ 0.855
8	1.595	0.161	1.756	2.732	+ 0.976
9	1.576	0.161	1.737	2.732	+ 0.995
10	1.835	0.161	1.996	2.732	+ 0.736
11	1.929	0.161	2.090	2.732	+ 0.642
12	1.900	0.161	2.061	2.732	+ 0.671
13	1.952	0.161	2.113	2.732	+ 0.619
14	1.515	0.161	1.676	2.732	+ 1.056
15–16	4.368	0.322	4.690	5.464	+ 0.774
17–18	3.889	0.322	4.211	5.464	+ 1.253
19	2.030	0.161	2.191	2.732	+ 0.541
		50% Increase in Diet.			
20	2.594	0.247	2.841	4.104	+ 1.263
21–22	5.545	0.494	6.039	8.208	+ 2.169
23–24	5.535	0.494	6.029	8.208	+ 2.179
25–26	5.183	0.494	5.677	8.208	+ 2.531
27	2.655	0.247	2.902	4.104	+ 1.202
		100% Increase in Diet.			
28	3.682	0.256	3.938	5.464	+ 1.526
29–30	7.858	0.512	8.370	10.928	+ 2.558
31–32	7.286	0.512	7.798	10.928	+ 3.130
33–34	8.577	0.512	9.089	10.928	+ 1.839
35–36	7.606	0.512	8.118	10.928	+ 2.810
37–38	8.560	0.512	9.072	10.928	+ 1.856
39–40	8.283	0.512	8.795	10.928	+ 2.133
41–42	8.762	0.512	9.274	10.928	+ 1.654
43–44	8.592	0.512	9.104	10.928	+ 1.824
		Normal Diet.			
45–46	4.920	0.634	5.554	5.464	— 0.090
47	2.435	0.317	2.752	2.732	+ 0.020

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TABLE IV (*continued.*)

Day.	N in urine. Grams.	N in hair, feces and cage wash. Gram.	Total N output. Grams.	N in food. Grams.	N balance.
		Second Fast.			
1	1.081	0.054	1.135	...	— 1.135
2	1.197	0.054	1.251	...	— 1.251
3	1.209	0.054	1.263	...	— 1.263
4	1.202	0.054	1.256	...	— 1.256
5	1.251	0.054	1.305	...	— 1.305
6	1.471	0.054	1.525	...	— 1.525
7	1.128	0.054	1.182	...	— 1.182
8	1.368	0.054	1.422	...	— 1.422
9	1.218	0.054	1.272	...	— 1.272
10	1.194	0.054	1.248	...	— 1.248
11	1.158	0.054	1.212	...	— 1.212
12	1.332	0.054	1.386	...	— 1.386
13	1.357	0.054	1.411	...	— 1.411
14	1.182	0.054	1.236	...	— 1.236
15	1.207	0.054	1.261	...	— 1.261
16	1.344	0.054	1.398	...	— 1.398
17	1.119	0.054	1.273	...	— 1.273
18	1.193	0.054	1.247	...	— 1.247
19	1.335	0.054	1.389	...	— 1.389
20	1.257	0.045	1.311	...	— 1.311
21	1.221	0.054	1.275	...	— 1.275
22	1.203	0.054	1.257	...	— 1.257
23	1.315	0.054	1.369	...	— 1.369
24	1.216	0.054	1.270	...	— 1.270
25	1.145	0.054	1.199	...	— 1.199
26	1.126	0.054	1.180	...	— 1.180
27	1.495	0.054	1.549	...	— 1.549
28	1.519	0.054	1.573	...	— 1.573
29	2.089	0.054	2.143	...	— 2.143
30	2.298	0.054	2.352	...	— 2.352

TABLE V.—BODY WEIGHT AND CREATININE COEFFICIENT.

Day.	Body weight. Kgs.	Gross gain or loss. Kgs.	Daily gain or loss. Kgs.	Per cent. gross gain or loss.	Per cent. daily gain or loss.	Creatinine coefficient.
			Preliminary Period.			
6	3.42	...	...	...	...	0.013
7	3.40	...	...	...	...	0.012
8	3.41	...	...	...	...	0.012
			First Fast.			
1	3.26	— 0.15	— 0.15	—4.40	—4.40	0.009
2	3.19	— 0.22	— 0.07	6.45	2.15	0.009
3	3.13	— 0.28	— 0.06	8.21	1.88	0.009
4 } 5	2.95	— 0.46	— 0.18	13.49	5.75	0.011
6	2.91	— 0.50	— 0.04	14.66	1.35	0.008
7	2.86	— 0.55	— 0.05	16.13	1.72	0.010

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TABLE V (*continued*).

Day.	Body weight. Kgs.	Gross gain or loss. Kgs.	Daily gain or loss. Kg.	Per cent. gross gain or loss.	Per cent. daily gain or loss.	Creatinine coefficient.
			First Fast.			
8	2.77	— 0.64	— 0.09	18.77	3.15	0.009
9 } 10 }	2.60	— 0.81	— 0.17	23.75	6.14	0.010
11	2.49	— 0.92	— 0.11	26.98	4.23	0.009
12	2.31	— 1.10	— 0.18	32.26	7.23	0.008
13	2.22	— 1.19	— 0.09	34.60	3.90	0.007
14	2.05	— 1.36	— 0.17	39.88	7.66	0.005
15	1.85	— 1.56	— 0.20	45.75	9.75	0.008
			Feeding Periods.			
			Preliminary.			
1	1.95	+ 0.10	+ 0.10	+ 6.41	+ 5.40	0.005
2	2.25	+ 0.40	+ 0.30	25.63	15.38	0.006
3	2.35	+ 0.50	+ 0.10	32.04	4.44	0.006
4	2.24	+ 0.39	— 0.11	24.99	— 4.68	0.006
			Normal Diet.			
5	2.20	+ 0.35	— 0.04	22.43	— 1.78	0.006
6	2.12	+ 0.27	— 0.08	17.30	— 3.64	0.008
7	2.19	+ 0.34	+ 0.07	21.80	+ 3.30	0.008
8	2.24	+ 0.39	+ 0.05	24.99	2.28	0.008
9	2.25	+ 0.40	+ 0.01	25.63	0.45	0.008
10	2.26	+ 0.41	+ 0.01	26.27	0.44	0.009
11	2.27	+ 0.42	+ 0.01	26.91	0.44	0.009
12	2.29	+ 0.44	+ 0.02	28.20	0.88	0.008
13	2.28	+ 0.43	— 0.01	27.56	— 0.44	0.008
14	2.31	+ 0.46	+ 0.03	29.48	+ 1.31	0.008
15	2.34	+ 0.49	+ 0.03	31.40	1.29	0.010
16	2.36	+ 0.51	+ 0.02	32.68	0.85	0.010
17	2.36	+ 0.51	0.00	32.68	0.00	0.009
18	2.36	+ 0.51	0.00	32.68	0.00	0.009
19	2.38	+ 0.53	+ 0.02	33.96	0.85	0.011
			50% Increase in Diet.			
20	2.42	+ 0.57	+ 0.04	+36.53	+1.68	0.011
21	2.49	+ 0.64	+ 0.07	41.01	2.89	0.011
22	2.50	+ 0.65	+ 0.01	41.65	0.40	0.010
23	2.57	+ 0.72	+ 0.07	46.14	2.80	0.011
24	2.61	+ 0.76	+ 0.04	48.70	1.55	0.011
25	2.63	+ 0.78	+ 0.02	49.98	0.77	0.012
26	2.67	+ 0.82	+ 0.04	52.55	1.52	0.011
27	2.75	+ 0.90	+ 0.08	57.67	3.00	0.013
			100% Increase in Diet.			
28	2.84	+ 0.99	+ 0.09	63.44	3.27	0.013
29	2.85	+ 1.00	+ 0.01	64.08	0.35	0.012
30	2.92	+ 1.07	+ 0.07	68.57	2.45	0.012
31	3.00	+ 1.15	+ 0.08	73.70	2.74	0.012
32	3.00	+ 1.15	0.00	73.70	0.00	0.012

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TABLE V (*continued*).

Day.	Body weight. Kgs.	Gross gain or loss. Kgs.	Daily gain or loss. Kg.	Per cent. gross gain or loss.	Per cent. daily gain or loss.	Creatinine coefficient.
			100% Increase in Diet.			
33	3.09	+ 1.24	+ 0.09	79.46	3.00	0.013
34	3.10	+ 1.25	+ 0.01	80.10	0.32	0.012
35	3.20	+ 1.35	+ 0.10	86.50	3.22	0.012
36	3.24	+ 1.39	+ 0.04	89.08	1.25	0.012
37	3.32	+ 1.47	+ 0.08	94.20	2.47	0.013
38	3.35	+ 1.50	+ 0.03	96.12	0.90	0.013
39	3.40	+ 1.55	+ 0.05	99.33	1.49	0.013
40	3.46	+ 1.61	+ 0.06	103.17	1.76	0.012
41	3.50	+ 1.65	+ 0.04	105.74	1.16	0.013
42	3.52	+ 1.67	+ 0.02	107.02	0.57	0.013
43	3.56	+ 1.71	+ 0.04	109.58	1.14	0.013
44	3.59	+ 1.74	+ 0.03	111.50	0.84	0.012
			Normal Diet.			
45	3.56	+ 1.71	— 0.03	109.58	— 0.83	0.011
46	3.54	+ 1.69	— 0.02	108.30	— 0.56	0.012
47	3.54	+ 1.69	0.00	108.30	0.00	0.011
			Second Fast.			
1	3.42	— 0.12	— 0.12	— 3.39	— 3.39	0.009
2	3.32	— 0.22	— 0.10	6.21	2.92	0.009
3	3.26	— 0.28	— 0.06	7.91	1.81	0.009
4	3.11	— 0.43	— 0.15	12.15	4.60	0.010
5	3.07	— 0.47	— 0.04	13.28	1.28	0.010
6	..	..	..	..	..	...
7	3.05	— 0.49	— 0.02	13.84	0.65	0.009
8	2.95	— 0.59	— 0.10	16.66	3.28	0.009
9	2.89	— 0.65	— 0.06	18.36	2.03	0.009
10	2.86	— 0.68	— 0.03	19.21	1.04	0.009
11	2.80	— 0.74	— 0.06	20.90	2.10	0.008
12	2.77	— 0.77	— 0.03	21.75	1.07	0.010
13	2.72	— 0.82	— 0.05	23.16	1.80	0.009
14	2.68	— 0.86	— 0.04	24.29	1.47	0.009
15	2.64	— 0.90	— 0.04	25.42	1.49	0.009
16	2.58	— 0.96	— 0.06	27.12	2.27	0.008
17	2.51	— 1.03	— 0.07	29.09	2.71	0.006
18	2.49	— 1.05	— 0.02	29.66	0.79	0.008
19	2.45	— 1.09	— 0.04	30.79	1.60	0.008
20	2.40	— 1.14	— 0.05	32.20	2.04	0.008
21	2.37	— 1.17	— 0.03	33.05	1.25	0.007
22	2.36	— 1.18	— 0.01	33.33	0.42	0.006
23	2.31	— 1.23	— 0.05	34.74	2.12	0.006
24	2.21	— 1.33	— 0.10	37.57	4.33	0.005
25	2.18	— 1.36	— 0.03	38.42	1.35	0.005
26	2.15	— 1.39	— 0.03	39.26	1.37	0.006
27	2.11	— 1.43	— 0.04	40.39	1.86	0.006
28	2.05	— 1.49	— 0.06	42.09	2.84	...
29	1.97	— 1.57	— 0.08	44.35	3.90	...
30	1.91	— 1.63	— 0.06	46.04	..	...

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TABLE VI.—NITROGEN IN DIET, FECES, HAIR AND CAGE WASHINGS.

	Preliminary period. 11 days.	First fast. 15 days.	Feeding periods. Pre-liminary. 4 days.	Normal. 15 days.	50% increase. 8 days.	100% increase. 17 days.	Normal. 3 days.	Second fast. 30 days.
Food (per day).								
Meat.....	2.533	..	3.618*	2.533	3.799	5.066	2.533	..
Crackers.....	0.1977	..	2.930*	0.1977	0.303	0.395	0.1977	..
Lard.....	0.0008	..	0.003*	0.0008	0.0012	0.002	0.0008	..
Bone ash....	0.0003	..	0.003*	0.0003	0.0005	0.0005	0.0003	..
Total (grams)	2.732	..	6.554*	2.732	4.104	5.464	2.732	..
H_2O.....	250 cc.	250 cc.	250 cc.	250 cc.	250 cc.	250 cc.	250 cc.	250 cc.
Feces.								
Grams.....	41.89	3.5	76.6		61.0	92.0	20.0	9.6
Wt. of N.....	1.691	0.309	2.143		1.596	3.540	0.739	0.776
% N.....	4.037	8.874	2.798		2.616	3.839	3.695	8.100
Gms.N per day	0.154	0.021	0.113		0.199	0.208	0.269	0.026
Hair.								
Grams.....	5.0			13.0				6.0
Wt. of N.....	0.575			1.555				0.666
% N.....	11.50			11.961				11.100
Gms.N per day	0.052			0.025				0.022
Cage washings.								
Wt. of N.....	0.326	0.268		1.084 (47 days)				0.189
Gms.N per day	0.029	0.0178		0.023				0.006
Total Nitrogen Excreted.								
Grams.....	2.592	..	..		..	..	..	..
Gram per day	0.235	0.064	0.161		0.247	0.256	0.317	0.054

muscle was but slightly lowered. This pronounced decrease of creatine found by us in fasting muscle is a most significant fact and shows clearly that in fasting we can not, with accuracy, consider the total amount of excreted creatine as resulting from the complete and permanent disintegration of muscular tissue. It appears that the creatine of the urine is derived either from disintegrating muscular tissue or is *removed in some manner from such tissues which are still functioning within the body.*

12. As a result of our experiments we have shown that in repeated fasting there is a slower and less profound tissue disintegration during the second fast, indicating a greater resistance of the body, acquired as a result of the initial fast. This increased resistance, noted in our experiments, following fasting may indicate that the "repeated fast," if properly regulated, may possess important therapeutic properties. The greater length of the second fast could not have been due to increased fat stores, for the fat present in the body of the animal at the beginning of the second fast was, according to our calculations, only fifty grams more than at the beginning of the first fast.

* Total weight of nitrogen fed during the four days.

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PHENYL ETHER AND SOME OF ITS DERIVATIVES (ADDENDUM).[2]

BY ALFRED N. COOK.

Bromination of p-Tolyl Ether.—The tetrabromo derivative was prepared by cautiously adding an excess of bromine in direct sunlight to

[1] These references were obtained from the English translation of Pashutin's book, prepared under the direction of Francis G. Benedict of the Carnegie Institution.

[2] Omitted by mistake from the article in the October number of THIS JOURNAL.

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the ether dissolved in carbon disulphide, while warming on the water bath. The resulting red viscous substance obtained was treated as in case of tetrabromophenyl ether. On distil ing, a large amount of char was formed and the yield of tetrabromo-*p*-tolyl ether was small. It is a light yellow, viscous substance which crystallizes in radial aggregations on cooling *per se* and is quite identical in appearance with tetrabromo-*m*-tolyl ether. It boils at 310–330° under 40 mm. pressure. It is soluble in carbon disulphide and petroleum ether, but insoluble in alcohol and most ordinary organic solvents. On analysis it yielded 62.64 per cent. of bromine. Calculated for $(CH_3.C_6H_2Br_2)_2O$, 62.69 per cent. No compound with a higher per cent. of bromine could be prepared even with the aid of iodine as a carrier.

Bromine was gradually added to some *p*-tolyl ether heated, *per se*, to 150° in quantity to form the dibromo compound. On distillation a large amount of char resulted and there was obtained a small yield of dibromo-*p*-tolyl ether.

These two substances were boiled with water, caustic alkalies, water and calcium carbonate and sodium carbonate but no reaction could be obtained, which would indicate that the bromine had entered the nucleus.

Bromination of o-Tolyl Ether.—Since only a few grams of *o*-tolyl ether were obtained from the distillation of a kilogram of *o*-cresolate of aluminium, there was not sufficient material available for repeated attempts to prepare the bromine derivatives. The *o*-tolyl ether was undoubtedly much less pure than in case of the other ethers and the reactions were much less clear cut. Considerable char resulted on distilling the bromine derivatives and in one or two cases nothing but char was obtained. However, substances were obtained which contained bromine in amounts which corresponded more nearly to the dibromo and tetrabromo compounds than anything else, *e. g.*, in brominating the ether with a large excess of bromine in the presence of iodine there was obtained a substance which boiled at about 300° and which yielded results on analysis ne rly 8 per cent. too low in bromine or the tetrabromo compound. However, while the reactions were not clear cut and the results unsatisfactory so far as obtaining pure compounds was concerned, it is evident that the bromine enters the nucleus and not the side chain, since on boiling for a long time with water, caustic alkalies, and water and calcium carbonate, the filtrate yielded no precipitate with silver nitrate.

VERMILION, S. D.

NOTE.

Note: Paraffin Hydrocarbons in Soils.—Through the kindness of Dr. F. B. Power, Director of the Wellcome Chemical Research Laboratories, of

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London, we have been able to compare a sample of our hydrocarbon obtained from soils[1] with a sample of the same hydrocarbon obtained from vegetable sources. A mixture of the two substances melts at 68°, the same temperature as the melting point of either one alone. This establishes conclusively the identity of the two compounds.

OSWALD SCHREINER AND EDMUND C. SHOREY.

NEW BOOKS.

A Text Book of Organic Chemistry. By WILLIAM A. NOYES. Professor of Chemistry in the University of Illinois. Second Edition. New York: Henry Holt and Company. 537 pp. Price, $1.50.

The new edition of this introduction to organic chemistry is written along the same lines as its predecessor. The most unique feature of the text is the radical departure from the general method of treatment of the subject, and the dropping of the division of organic chemistry into fatty and organic compounds. An attempt has been made to bring the book up to date, and considerable new and interesting material has been added. Less material however is presented than in other introductory text books of organic chemistry.

The chapter on Compounds of Interest in Physiology and Pathology has been rewritten on the basis of the classification of proteins recently adopted by the American Society of Biological Chemists and the American Physiological Society.

Owing to the overwhelming and increasing mass of chemical data at the disposal of a writer it might be expected that some errors will appear in a text of this character. There is one misstatement however in this book to which the reviewer is compelled to call attention. He was certainly surprised to read on page 295 that "*uracil* the mother substance of uric acid has not been prepared." This pyrimidine was first synthesized by Fischer and Roeder in 1901 (*Ber. chem. Ges.*, **34**, 3751) and later by Wheeler and Merriam in 1903 (*Am. Chem. J.*, **29**, 478). The latest paper on the synthesis of this compound was published by Wheeler and Liddle in 1908 (*Am. Chem. J.*, **40**, 547).

The reviewer also desires to call attention to pages 306 and 307, where the author states that ethyl cyanate is formed by the action of cyanogen chloride on sodium ethylate and that the ester is decomposed by alkali giving alcohol and potassium cyanate. A student would naturally conclude from these statements that the oxygen esters of cyanic acid HNCO are capable of existence. The statement is evidently based on the statements in Beilstein's Handbuch, **1**, 1266–7, but the author has evidently overlooked the fact that Nef (*Ann.*, **287**, 310) examined the

[1] THIS JOURNAL, 33, 82.

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behavior of cyanogen chloride towards sodium alcoholate and showed that they combine, giving diethyl iminocarbonate $HN:C(OC_2H_5)_2$. He states: "Die wirklichen Ester der normalen Cyansäure sind bislang nicht bekannt." See also Beilstein's "Handbuch" (Ergänzungsband), Vol. I, p. 719, and Richter's "Organische Chemie," Vol. I, p. 510 (edition of 1909).

The author believes that a satisfactory knowledge of organic chemistry cannot be acquired from a text-book alone and recommends a large amount of laboratory work. This is a commendable view. In order to aid the instructor in directing experimental work a series of preparations is appended to each chapter of the book. T. B. JOHNSON.

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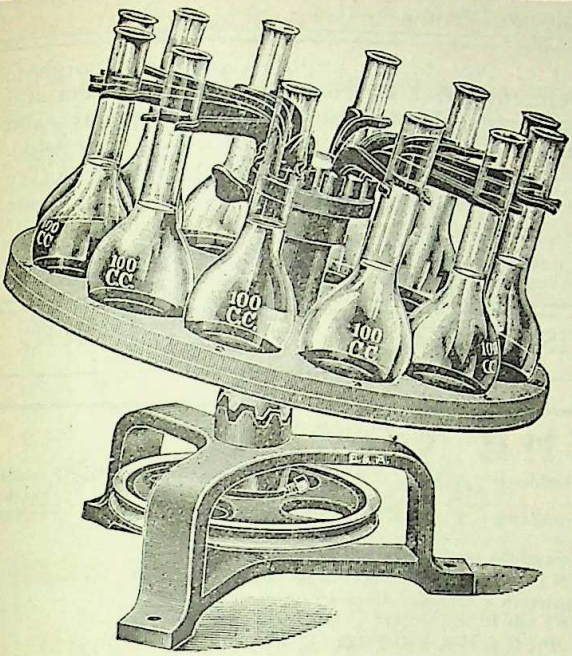
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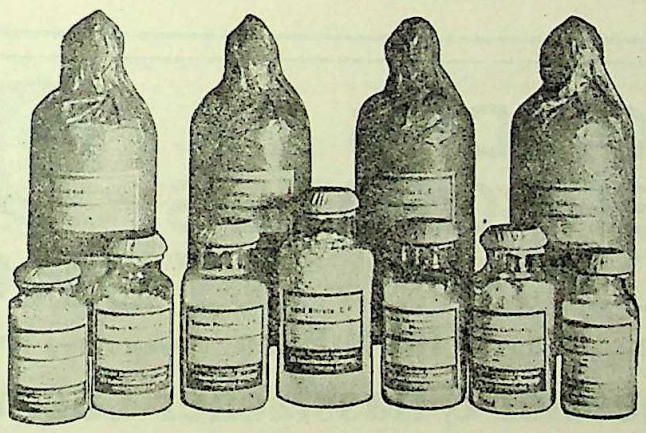
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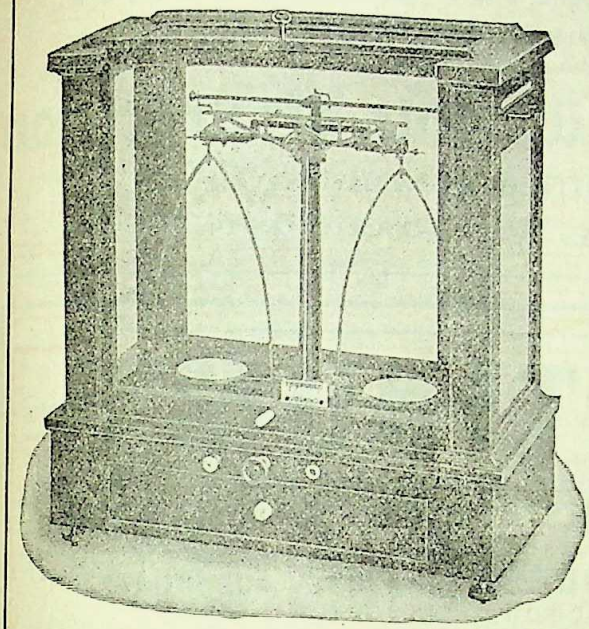
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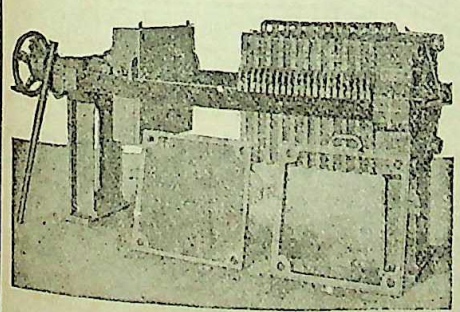
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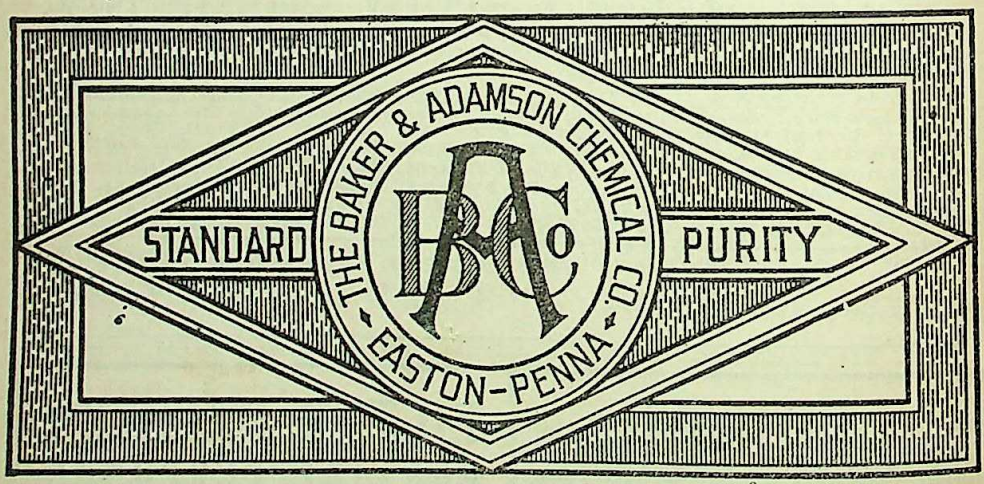
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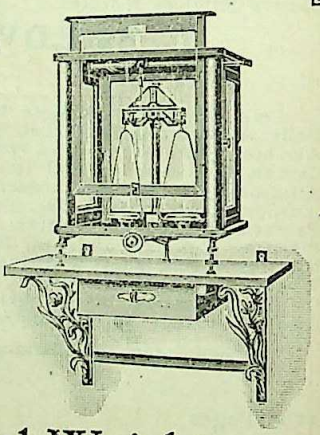
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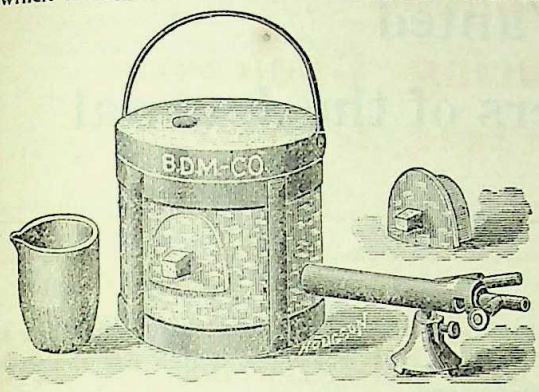
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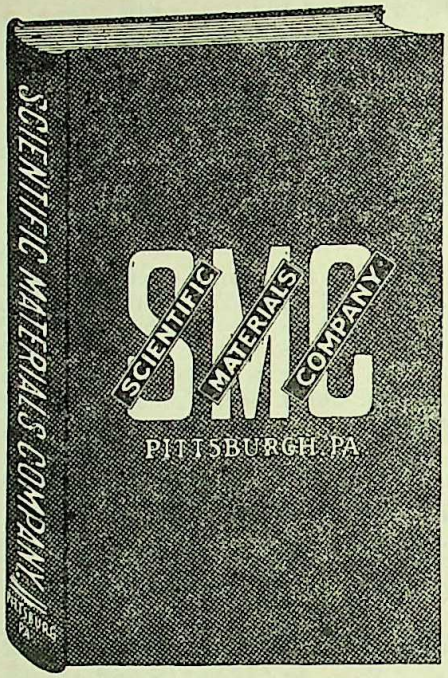
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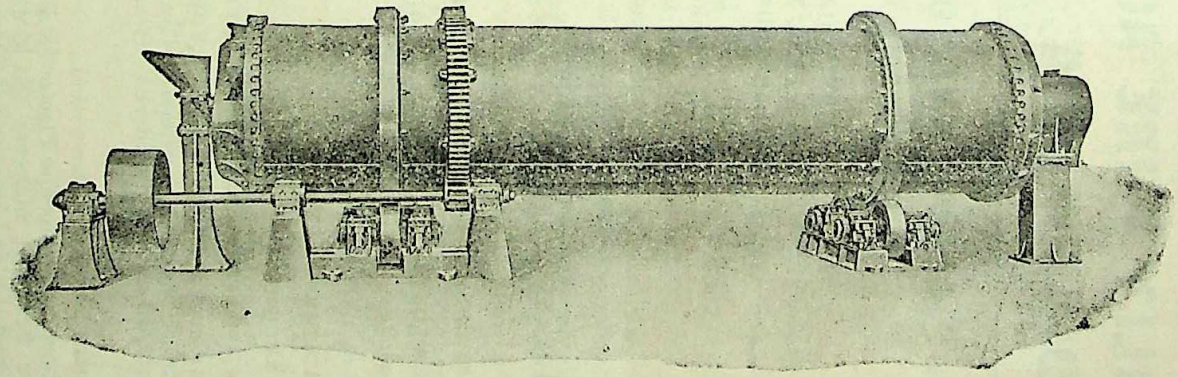
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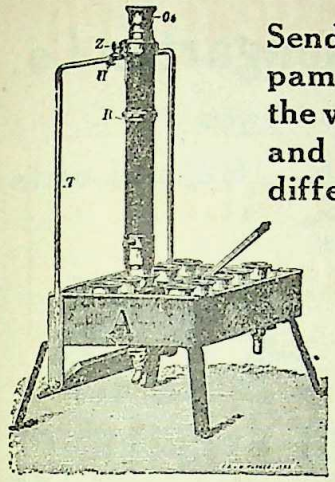
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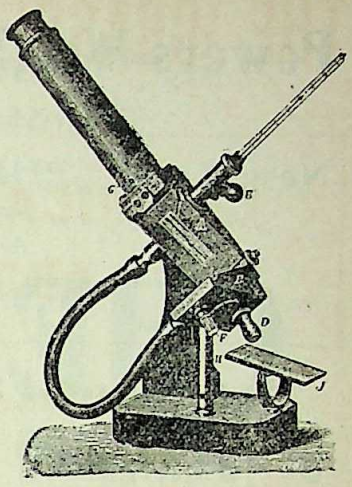
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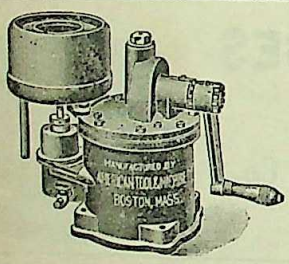
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White, Wm. R., 314 Hancock St., Nashville, Tenn.
Wilker, Arthur V., Berea, Ohio.
Wilson, Ernest D., 1521 B St., Lincoln, Nebr.
Woodbury, Carl V., Northfield, Vermont.

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Zimmerman, R. E., Technology Chambers, Boston, Mass.
Zimmerschird, Karl W., 616 Church St., Ann Arbor, Mich.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

MILWAUKEE SECTION.

The regular meeting of the Section was held on December 16th at the Hotel Blatz. The address of the evening was by Prof. S. W. Parr on "Spontaneous Combustion." There was a large attendance and the paper was one of the most instructive delivered before the Section. The usual informal dinner preceded the meeting.

A regular meeting was also held on January 31st, at the Hotel Blatz. The program of the evening was a discussion of specifications. Dr. C. B. Dudley's address on "The Making of a Specification" was read, after which several specifications were proposed and discussed. An informal dinner preceded the meeting.

BEN L. SALOMON, *Secretary.*

UNIVERSITY OF MICHIGAN SECTION.

The January meeting was held in the Chemical Building, Wednesday, January 11th, at 4.30 P.M. S. L. Bigelow gave an address "On the Function of the Walls in Capillary Phenomena." Short talks on various phases of the Minneapolis meeting were given by L. H. Cone, W. J. Hale, A. B. Stevens, H. H. Willard.

WILLIAM G. SMEATON, *Secretary.*

INDIANA SECTION.

The regular meeting of the Section was held in the office of the State Food and Drug Laboratory, Indianapolis, Friday evening, January 13th.

Mr. F. B. Wade read a paper on "Precious Stones, Their Imitations, Artificial Production and Methods Employed in Cutting." The paper was illustrated with stereopticon views.

The Section met in the office of the State Food and Drug Laboratory, Friday evening, February 10th.

Papers were read by George Spitzer, of Lafayette, Ind., on "The Quantitative Determinations by the Spectrophotometer," and by W. M. Blanchard, of Greencastle, Ind., on "A Brief University Extension Course in General Chemistry."

A. D. THORBURN, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

At the meeting of the Section on January 17th, the following papers were presented by P. B. Hawk. (1) "Post-Anesthesia Glycosuria." (2) "Urine Formation during Ether Anesthesia." Reports of the Minneapolis meeting of the Society were given by Professors Noyes and

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Parr and of the New Haven meeting of the Biological Chemists by Professor Hawk.

GRINNELL JONES, *Secretary.*

PHILADELPHIA SECTION.

The January meeting of the Section was held in the main lecture room of the John Harrison Laboratory of Chemistry, Philadelphia, Pa., on Thursday, January 19th.

The program consisted of a lecture on "Modern Refrigerating and Ice-Making Machinery and Processes" by Dr. Charles H. Ehrenfeld, professor of chemistry and physics at York Collegiate Institute, York, Pa., and chief chemist of the York Manufacturing Co. The lecture was well illustrated and an actual demonstration given with heavy machinery showing on a small scale how artificial ice is made commercially by the use of liquid ammonia. Liquid ammonia was shown in a suitable glass container. The attendance was large, about 200 being present.

C. S. BRINTON, *Secretary.*

COLUMBUS SECTION.

The Section met in the Chemical Lecture Room, Ohio State University January 19th.

The program consisted of the following discussions: "An Important Method for the Preparation of Orthohydroxyazo Compounds," by Professor Wm. McPherson and Cecil Boord, presented by Mr. Boord. "The Action of the Derivatives of Tolylhydrazines on Quinones," by Professor Wm. McPherson and George W. Stratton, presented by Mr. Stratton. Professor McPherson then outlined the aims of these researches. This was followed by accounts of impressions and personal observations of the recent Minneapolis meetings by Messrs. McPherson, Henderson, Patterson and Withrow.

JAMES R. WITHROW, *Secretary.*

PITTSBURG SECTION.

At the December meeting of the Section the following officers were elected for the year 1911: *President*, Dr. J. K. Clements; *Vice-Chairman*, Dr. W. O. Snelling; *Secretary*, Dr. C. C. Vogt; *Councilors*, Dr. F. C. Phillips, Dr. J. O. Handy.

The regular meeting of the Section was held on Thursday evening, January 19th, at 8 o'clock.

The following program was presented: "The Rate of Decomposition of Limestone," by W. E. Emley. Informal reports on the Minneapolis meeting were made by Messrs. I. C. Allen and J. K. Clement.

C. C. VOGT, *Secretary.*

MINNESOTA SECTION.

The January meeting of the Section was held in the Chemical Laboratory of the University of Minnesota on Friday evening, January 20th. Reports were presented from the committees in charge of the winter

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meeting of the Society. Reviews of certain papers presented at the winter meeting of the American Chemical Society were given by Messrs. P. H. M.-P. Brinton, B. F. P. Brenton, F. W. Bliss and V. H. Roehrich.

FRANCIS C. FRARY, *Secretary.*

LOUISIANA SECTION.

The forty-sixth meeting was held at the Directors' Room of the Board of Trade, New Orleans, on Friday, January 20th, at 8 P.M.

The following officers were elected to serve for the ensuing year: *President*, Dr. Philip Asher; *Vice-President*, Dr. B. P. Caldwell; *Secretary-Treasurer*, Mr. G. B. Taylor; *Councilor*, Dr. Chas. E. Coates.

The retiring president and the secretary made their annual reports to the Society.

A series of five-minute talks by the members on chemical subjects was successfully inaugurated.

GEORGE B. TAYLOR, *Secretary.*

KANSAS CITY SECTION.

The following officers were elected at the December meeting for the year 1911: *President*, F. B. Dains; *Vice-President*, L. D. Havenhill; *Secretary-Treasurer*, E. A. White; *Assistant Secretary*, H. J. Broderson; *Councilor*, E. H. S. Bailey.

The January meeting was held at the University of Kansas, Lawrence, on Saturday evening, January 21st, beginning at 5 o'clock.

The program was as follows: "Some Experiments with the Atwater Rosa Calorimeter," by Stanley D. Wilson. Dinner, to which all were invited. "The Electrolysis of Copper Sulfate in Acid Solution with Continuous, Interrupted and Alternating Currents," by L. V. Redman.

E. A. WHITE, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club, on Thursday evening, January 26th. Dinner was served promptly at 7 o'clock. The speaker for the evening was Mr. C. E. Swett, of Providence, who addressed the Section on "Applied Chemistry in the Jewelry Industry."

ALBERT W. CLAFLIN, *Secretary.*

NASHVILLE SECTION.

Under the charter granted to the Nashville Section on January 5th, an organization meeting was held at Furman Hall, Vanderbilt University, on January 26th. A constitution was adopted and the following officers were elected: W. L. Dudley, *Chairman*; J. I. D. Hinds, *Vice-Chairman*; R. W. Balcom, *Councilor*; L. J. Desha, State Food and Drugs Inspection, Nashville, *Secretary* and *Treasurer*. After the completion of this business Dr. Dudley gave an informal talk on "Action of Wireless Waves on Rarefied Gases."

L. JUNIUS DESHA, *Secretary.*

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NORTH CAROLINA SECTION.

The midwinter meeting of the Section was held in the Agricultural Building at Raleigh, on January 28th, at eleven o'clock in the morning.

The following officers were chosen for the ensuing year: *President*, G. M. MacNider; *Vice-President*, L. B. Lockhart; *Secretary-Treasurer*, B. J. Ray; *Councilor*, J. E. Mills; *Reporters*, L. F. Williams, R. A. Hall.

The following papers were presented together with a skeleton outline by R. A. Hall on "The Determination of the Neutrality of Ammonium Citrate." Presidential address, W. M. Allen. "Some Sources of Inaccuracy in the Tiemann-Schultz Method," by W. A. Withers and F. W. Sherwood. "The Determination of Sulfur in Condimental Feeds," by G. M. MacNider. "The Relation of Viscosity and Distillation Tests to the Quality of Illuminating Oils," by L. B. Lockhart and Manlius Orr. "The Quality of Commercial Gasoline," by L. B. Lockhart and Manlius Orr. "The Teaching of Chemistry in the High Schools of North Carolina," "The Nature of Mass," "The Relation of Temperature and Molecular Attraction," by J. E. Mills.

B. J. RAY, *Secretary*.

SECTION OF WESTERN NEW YORK.

A special meeting was held at the Buffalo Central Y. M. C. A. auditorium, on Tuesday evening, January 31st, at 8.15 o'clock, under the joint auspices of Buffalo Academy of Medicine, Western N. Y. Section of American Chemical Society, Erie County Medical Society, Erie County Pharmaceutical Association.

Harvey W. Wiley, Ph.D., M.D., LL.D., Chief, Bureau of Chemistry, Washington, D. C., the noted pure food expert, spoke on "The Public Health—Our Greatest National Asset."

WALTER WALLACE, *Secretary*.

CHICAGO SECTION.

An informal meeting was held Friday, February 3rd, at Kuntz-Rembler's, 305 Wabash Avenue. The meeting was in honor of Dr. Alexander Smith, recently elected president of the Society. Dinner was served at 6.30. Informal talks began at 8 P.M.

The February meeting was held in the rooms of the Western Society of Engineers, on Friday evening, February 17th, at 8 P.M., preceded by the usual informal dinner.

The general subject of the evening was the potash situation, giving "The American View-Point," by Mr. C. H. McDowell, Armour & Co., Chicago, and "The German View-Point," by Mr. H. A. Huston, German Kali Works, Baltimore.

Mr. W. D. Richardson introduced the subject. Mr. Fred Rayfield and Mr. C. A. Alling, among others, discussed the subject of the meeting.

D. K. FRENCH, *Secretary*.

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CLEVELAND SECTION.

A meeting of the Section was held at the University Club, on Saturday evening, February 4th. An informal dinner was served at 6.30 P.M., followed by a lecture on "Recent Developments in Electro Chemistry in Norway and Sweden," by Prof. J. W. Richards, of Lehigh University, and a "Report on the Minneapolis Meeting," by Mr. H. D. Batchelor, of the National Carbon Co.

W. R. VEAZEY, *Secretary.*

CINCINNATI SECTION.

The 166th regular meeting of this Section was held on Wednesday evening, February 8th, at the Ohio Mechanics Institute.

The special topic of discussion for the evening was "Ehrlich and His Work in Special Therapy." Papers on this subject were given by Dr. O. Berghausen and Dr. E. B. Reemelin, followed by informal discussion.

ALFRED SMITH, *Secretary.*

WASHINGTON SECTION.

The 204th meeting was held at the Cosmos Club, Thursday, February 9th, at 8 P.M.

The following program was presented: "Chlorsprodiosite," by Frank Cameron, W. H. Waggaman and W. J. McCaughey, Bureau of Soils. "Calculation of the Rate of Increase in Temperature of Fruits under Adiabatic Conditions," by H. C. Gore, Bureau of Chemistry. "Some Phases of Drug Work" (illustrated with lantern slides), by L. F. Kebler, Bureau of Chemistry. "Exhibition of the Process of Welding by Thermite," by P. R. McCrary, assisted by J. J. Enright (by invitation).

H. S. BAILEY, *Secretary.*

SECTION OF EASTERN NEW YORK.

The regular meeting for February was held at the Rensselaer Polytechnic Institute, Troy, on Friday evening, February 10th, at 8.15 o'clock.

The following paper was presented: "Notes on Water Supply," by Dr. William P. Mason, of Rensselaer Polytechnic Institute.

After the address a report was heard from the Committee on Sewage Disposal. The appointment of this committee is the first outcome of a suggestion that active interest be taken in the practical problems of a chemical nature confronting the towns of the Section.

G. R. FONDA, *Secretary.*

NEW YORK SECTION.

The fifth regular meeting of the session of 1910–'11 was held at the Chemists' Club, on February 10th.

The following papers were presented: "The Hydrate Theory," by A. T. Lincoln. "Determination of Total Solids in Milk," by Paul Poetschke. "Milk Costs," by W. E. J. Kirk. "Raw and Pasteurized Milk and Milk Serums," by Edward Gudeman.

C. M. JOYCE *Secretary.*

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NORTHEASTERN SECTION.

The one hundred and first regular meeting of the Section was held Friday, February 17th, at 8 o'clock P.M., at the Twentieth Century Club, Boston, preceded by the usual dinner.

Dr. Francis G. Benedict, director of the nutrition laboratory of the Carnegie Institution, addressed the Section upon "The Influence of Mental and Muscular Work on Nutritive Processes."

Dr. E. Weintraub, head of the research laboratory of the General Electric Company at West Lynn, presented a paper on "Boron: Its Preparation on a Large Scale and its Properties."

WARREN K. LEWIS, *Secretary.*

CALIFORNIA SECTION.

The fifty-sixth regular meeting of the Section was held on Saturday evening, February 18th, at 8 o'clock, at Bergez and Franks' Café, preceded by the usual dinner. The paper of the evening was on "Fire Assay: Its Improvement during the Last Twenty Years," by Abbot A. Hanks.

CHARLES S. ASH, *Secretary.*

CORNELL SECTION.

The February meeting was held on Monday night, February 20th, at 8 o'clock in Morse Hall.

The program consisted of the following reports: "The Decomposition of Bromoform," by G. J. Sargent. "The Detection and Determination of Dihydroxystearic Acid in Soils," by J. K. Plummer. "Life in an Experiment Station," by L. J. Cross. "Tetrachlorgallein and Some of Its Derivatives," by Dr. W. R. Orndorff.

J. C. ANDREWS, *Secretary.*

DECEASED MEMBERS.

Carl Svanté Nicanor Hallberg, Chicago, Ill.
Arthur F. Hartman, Nappanee, Ind.
J. C. Hayward, Ithaca, N. Y.
Leonard P. Kinnicutt, Worcester, Mass.
Clifford J. Monahan, New Haven, Conn.
W. R. Quinan, West Somerset, Cape Colony, So. Africa.

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VOL. XXXIII. MARCH, 1911. No. 3.

THE JOURNAL

OF THE

American Chemical Society

EIGHTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1910.

BY F. W. CLARKE.

Received January 20, 1911.

During 1910 a number of important papers on atomic weights have appeared, and their results are summarized in the following pages. A third edition of Clarke's "Recalculation of the Atomic Weights," revised and much enlarged, was published by the Smithsonian Institution early in the year. The new data are as follows:

Hydrogen.—Atomic weight recalculated by Grinnell Jones[1] from all the trustworthy determinations. The value finally deduced is H = 1.00775. That found in Clarke's recalculation is 1.00779. The two agree to within one part in 25000.

Nitrogen.—Guye and Drouginine[2] have determined the atomic weight of nitrogen from analyses of weighed quantities of N_2O_4. A spiral of iron wire was heated electrically in the gas, and its increase in weight gave the amount of oxygen contained in the latter. The figures are as follows:

Weight N_2O_4.	Weight $2O_2$.	Weight N_2.	At. wt. N.
0.8856	0.6160	0.2696	14.005
1.8494	1.2860	0.5634	14.019
2.1281	1.4801	0.6480	14.010
1.7191	1.1957	0.5234	14.008
0.9951	0.6921	0.3030	14.010
1.5324	1.0658	0.4666	14.009
1.2425	0.8642	0.3783	14.008
		Mean,	14.010

[1] THIS JOURNAL, 32, 513.
[2] *J. chim. phys.*, 8, 473.

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Clarke's combination of all previous determinations gives N = 14.0101. Richards' value is distinctly lower.

Silver and Iodine.—The ratio between silver and iodine has been re-measured, with extreme care, by Baxter.[1] The corrected weights and ratio are subjoined.

Weight I.	Weight Ag.	Ratio Ag : I.
9.00628	7.65468	0.849927
13.45067	11.43179	0.849905
11.86648	10.08571	0.849933
8.52461	7.24498	0.849890
6.42840	5.46351	0.849902
8.30266	7.05641	0.849897
9.95288	8.45904	0.849909
6.97131	5.92591	0.849899
9.38852	7.97927	0.849897
6.56811	5.58231	0.849911
18.87136	16.03902	0.849913
17.84091	15.16249	0.849872
14.95666	12.71170	0.849902
		Mean, 0.849906

This mean, combined with that found by Baxter and Tilley[2] for the ratio $2Ag : I_2O_5$, 0.64230, gives Ag = 107.864 and I = 126.913. These values are remarkably low.

Lithium.—The peculiar merit of the work done by Richards and Willard[3] on the atomic weight of lithium, apart from its accuracy, is found in the fact that the ratios measured give values for Ag, Cl and Li which are independent of all previous investigations. Three ratios were measured: $LiClO_4$ to LiCl (or 4O : LiCl), Ag to LiCl, and AgCl to LiCl. To economize space I omit the "preliminary" series of determinations, and give below only those marked "final." Vacuum weights are given throughout.

RATIO 4O : LiCl.

Weight $LiClO_4$.	Weight LiCl.	Ratio.
12.79265	5.09744	1.50962
10.55416	4.20534	1.50970
11.39912	4.54205	1.50969
11.17008	4.45070	1.50974
17.84842	7.11167	1.50974
22.58273	8.99846	1.50962
	Mean,	1.50968

[1] THIS JOURNAL, 32, 1603.

[2] See 17th Report, *Ibid.*, 31, 257, 258.

[3] *Ibid.*, 32, 4.

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RATIO LiCl : Ag.

Weight LiCl.	Weight Ag.	Ratio.
5.82422	14.82035	0.392988
6.28664	15.99687	0.392991
5.82076	14.81122	0.392997
6.70863	17.07038	0.392998
6.24717	15.89620	0.392998
7.75349	19.72977	0.392984
7.99108	20.33415	0.392988
	Mean,	0.392992

RATIO LiCl : AgCl.

Weight LiCl.	Weight AgCl.	Ratio.
6.28662	21.25442	0.295779
5.82076	19.67873	0.295790
6.70863	22.68030	0.295791
6.24717	21.12073	0.295784
5.50051	18.59600	0.295790
8.34521	28.21438	0.295779
6.65987	22.51564	0.295789
	Mean,	0.295786

From these ratios, combined, Ag = 107.871, Cl = 35.454, and Li = 6.939. The authors regard the value for silver as representing the lower limit for that constant.[1]

Calcium.—Atomic weight redetermined by Richards and Hönigschmid,[2] from analyses of calcium bromide. Two ratios were measured, with the following results. Vacuum weights are implied. Values calculated with Ag = 107.88, Br = 79.916.

RATIO $CaBr_2$: 2Ag.

Weight $CaBr_2$.	Weight 2Ag.	At. wt. Ca.
4.20860	4.54252	40.068
4.58644	4.95025	40.071
5.34866	5.77301	40.068
7.23724	7.81126	40.073
4.67673	5.04779	40.068
7.41636	8.00455	40.074
	Mean,	40.0703

[1] Scheuer, *J. chim. phys.*, 8, 289, discusses the atomic weight of chlorine as deduced from the density of HCl. The paper is practically a reproduction of one cited last year. Hinrichs, *Compt. rend.*, 151, 513, argues that Ag = 108 exactly.

[2] THIS JOURNAL, 32, 1577. A second paper by the same authors is in THIS JOURNAL for January, 1911.

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RATIO $CaBr_2$: 2AgBr.

Weight $CaBr_2$.	Weight 2AgBr.	At. wt. Ca.
10.18591	19.13778	40.073
7.92400	14.88810	40.072
6.78048	12.73961	40.072
6.45970	12.13702	40.070
5.95390	11.18684	40.067
5.15998	9.69513	40.067
	Mean,	40.0702

Why this determination, which confirms the earlier work of Richards, should be so much lower than that of Hinrichsen is unexplained. The new work is probably to be preferred.

Strontium.—Thorpe and Francis[1] have redetermined the atomic weight of strontium by several distinct methods. The corrected weights are given in the following summary of results:

RATIO $SrBr_2$: 2Ag.

Weight $SrBr_2$.	Weight 2Ag.	Ratio.
1.77884	1.55073	1.1471
1.86109	1.62260	1.1470
1.85254	1.61511	1.1470
1.73801	1.51534	1.1470
1.85787	1.61994	1.1469
1.70563	1.48707	1.1470
	Mean,	1.1470

Hence Sr = 87.645.

RATIO $SrBr_2$: 2AgBr.

Weight $SrBr_2$.	Weight 2AgBr.	Ratio.
1.86112	2.82438	0.65895
1.85261	2.81155	0.65893
1.73807	2.63762	0.65895
1.85798	2.81999	0.65886
1.70571	2.58866	0.65892
	Mean,	0.65892

Hence Sr = 87.653.

RATIO $SrCl_2$: 2Ag.

Weight $SrCl_2$.	Weight 2Ag.	Ratio.
1.64759	2.24203	0.73486
1.66352	2.26356	0.73491
1.53462	2.08817	0.73491
1.64619	2.24011	0.73487
1.76006	2.39486	0.73493
1.56224	2.12572	0.73492
	Mean,	0.73490

Hence Sr = 87.642.

[1] *Proc. Roy. Soc.*, 83 (A), 277.

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RATIO $SrCl_2$: 2AgCl.

Weight $SrCl_2$.	Weight 2AgCl.	Ratio.
1.64764	2.97899	0.55309
1.66357	3.00762	0.55312
1.53467	2.77416	0.55314
1.64624	2.97653	0.55307
1.76010	3.18202	0.55314
	Mean,	0.55311

Hence Sr = 87.645.

Supplementary determinations were made by determining the ratios $SrBr_2$: $SrSO_4$, and $SrCl_2$: $SrSO_4$, as follows:

RATIO $SrBr_2$: $SrSO_4$.

Weight $SrBr_2$.	Weight $SrSO_4$.	Ratio.
7.14570	5.30466	1.3471
7.64281	5.67326	1.3472
9.86072	7.32047	1.3470
	Mean,	1.3471

Hence Sr = 87.629.

RATIO $SrCl_2$: $SrSO_4$.

Weight $SrCl_2$.	Weight $SrSO_4$.	Ratio.
7.30246	8.46071	0.86310
8.71628	10.09868	0.86311
8.46493	9.80743	0.86311
8.79502	10.18959	0.86314
	Mean,	0.863115

Hence Sr = 87.661.

The authors adopt 87.65 as their final value, after discussing the relative merits of the several ratios. The calculations are based upon Ag = 107.88, Cl = 35.46, Br = 79.916, and S = 32.07.

Mercury.—Easley[1] has continued his research upon the atomic weight of mercury, the first part of which was noticed last year. Mercuric chloride was analyzed by electrolysis, giving the subjoined results. The weights are reduced to a vacuum, and the calculations are based upon Cl = 35.46.

PRELIMINARY SERIES.

Weight $HgCl_2$.	Weight Hg.	At. wt. Hg.
10.05743	7.43123	200.68
8.41289	6.21687	200.71
10.99056	8.11897	200.52
10.28282	7.59681	200.58
19.57120	14.46032	200.65
	Mean,	200.63

[1] THIS JOURNAL, 32, 1117.

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FINAL SERIES.

Weight $HgCl_2$.	Weight Hg.	At. wt. Hg.
8.14695	6.01909	200.61
11.03881	8.15592	200.64
13.48192	9.96129	200.66
11.08026	8.18610	200.60
11.31231	8.35819	200.66
21.44026	15.84060	200.62
	Mean,	200.63

This confirms the previous work, and seems to prove that the heretofore accepted value for mercury is too low.

Phosphorus.—Atomic weight redetermined by Baxter and Jones[1] from analyses of silver phosphate.

Weight Ag_3PO_4.	Weight 3AgBr.	Ratio.
6.02166	8.34490	1.34558
6.35722	8.55419	1.34559
5.80244	7.80819	1.34567
5.05845	6.80685	1.34564
3.34498	3.43544 (AgCl)	1.34560
7.15386	9.62694	1.34570
7.20085	9.68947	1.34560
6.20182	8.34522	1.34561
5.20683	7.00605	1.34555
	Mean,	1.34562

In experiment 5 the silver was weighed as chloride, but recalculated to bromide in the ratio. With Ag = 107.88, P = 31.043.

Vanadium.—Prandtl and Bleyer, whose work on the atomic weight of vanadium was noticed in my report for 1909, have published a second memoir[2] on the subject. Eight new analyses of vanadyl trichloride are given, of which four are rejected as defective. The four satisfactory determinations follow, with vacuum weights, and the ratio 3AgCl : $VOCl_3$: : 100 : x.

Weight $VOCl_3$.	Weight 3AgCl.	Ratio.
7.77585	19.26836	40.301
8.41904	20.86554	40.311
10.66137	26.42699	40.321
5.53998	13.73492	40.333
	Mean,	40.3165

From these figures, combined with the earlier series, the authors deduce V = 51.061, ±0.024, when Ag = 107.880 and Cl = 35.460.

Prandtl and Bleyer also investigated the ratio V_2O_5 : V_2O_3, by re-

[1] THIS JOURNAL, 32, 298.

[2] *Z. anorg. Chem.*, 67, 257.

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duction of the pentoxide in hydrogen. Their determinations, with vacuum weights, appear in the next table.

Weight V_2O_5.	Weight V_2O_3.	At. wt. V.
9.11431	7.51639	51.261
9.85727	8.13127	51.376
8.70923	7.18456	51.395
12.26426	10.11721	51.394
	Mean,	51.3565 [1]

Although these determinations agree with Roscoe's, the authors regard them as doubtful. Their $VOCl_3$ determinations are preferred.

The work of McAdam[2] on this constant consisted in reducing $NaVO_3$ to NaCl by heating in dry HCl. With vacuum weights, and NaCl = 58.46, the following results were obtained:

Weight $NaVO_3$.	Weight NaCl.	At. wt. V.
4.8564	2.3277	50.966
5.6404	2.7033	50.976
4.4263	2.1220	50.946
5.7805	2.7710	50.952
9.4902	4.5478	50.997
	Mean,	50.967

Taking into consideration the determinations of Prandtl and Bleyer, the atomic weight of vanadium may be rounded off to 51.

Tantalum.—Balke's[3] determinations of the atomic weight of tantalum are based upon the hydrolysis of the pentachloride. With vacuum weights and Cl = 35.46, the final results are as follows:

Weight $TaCl_5$.	Weight Ta_2O_5.	At. wt. Ta.
12.99680	8.02326	181.49
9.24957	5.71104	181.60
10.17456	6.28133	181.52
17.99542	11.11014	181.55
11.70558	7.22693	181.55
6.24767	3.85658	181.46
7.26375	4.48398	181.48
15.88270	9.80465	181.49
	Mean,	181.52

The rounded-off number 181.5 is to be accepted.

Tellurium.—Marckwald and Foizik,[4] by a complex volumetric process, find for this atomic weight the value 127.61. The data are too bulky and complicated for reproduction here. The purpose of the investigation

[1] The authors give 51.374.
[2] THIS JOURNAL, 32, 1603.
[3] *Ibid.*, 32, 1127.
[4] *Ber.*, 43, 1710.

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was not so much to determin the atomic weight exactly, as to ascertain the cause of the low value found in several previous researches.

Flint[1] has continued the work reported by Browning and Flint in 1909 on the fractionation of tellurium by hydrolysis of the tetrachloride. The unfractionated material, by the basic nitrate method, gave Te = 127.45. Progressive diminution of the atomic weight was noted in a series of fractions, namely the fourth, eight and tenth. The tenth gave low atomic weights as shown in the following table:

Weight Te_2HNO_7.	Weight TeO_2.	At. wt. Te.
2.06311	1.71688	124.25
2.18903	1.82172	124.27
3.56161	2.96446	124.42
2.99821	2.49537	124.37
2.86977	2.38824	124.27
2.47403	2.05898	124.31
4.85363	4.03943	124.32
		Mean, 124.32

The investigation is still in progress; but the present results are promising, and seems to show that ordinary tellurium is really a mixture. If that should be proved, all former determinations of the atomic weight would go for nothing.

Scandium.—Preliminary determinations of the atomic weight of scandium, by the sulfate method, are given by Meyer and Winter,[2] but without the detailed weighings. The values found for Sc range between 44.86 and 45.37; in mean, 45.12. This is much higher than the accepted value.

Neodymium.—By very careful analyses of neodymium chloride, Baxter and Chapin[3] have determined the atomic weight of the metal. Two ratios were measured, with vacuum weights, and reduced with Ag = 107.880 and Cl = 35.457.

Ratio $NdCl_3$: 3Ag.

Weight $NdCl_3$.	Weight 3Ag.	At. wt. Nd.
4.27402	5.51855	144.283
2.79574	3.61030	144.249
2.77391	3.58196	144.259
3.42064	4.41695	144.267
4.11855	5.31786	144.280
3.95958	5.11289	144.266
4.64435	5.99699	144.271
		Mean, 144.268

[1] *Am. J. Sci.*, [4] 30, 209.
[2] *Z. anorg. Chem.*, 67, 398.
[3] *Proc. Am. Acad.*, 46, 215 (1910); reproduced in This Journal for January, 1911.

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RATIO $NdCl_3 : 3AgCl$.

Weight $NdCl_3$.	Weight 3AgCl.	At. wt. Nd.
3.16218	5.42546	144.257
2.93305	5.03226	144.262
2.99149	5.13195	144.289
2.62468	4.50338	144.250
2.38439	4.09064	144.278
2.55827	4.38891	144.280
3.59114	6.16095	144.277
4.27402	7.33203	144.293
4.69459	8.05444	144.264
2.79574	4.79630	144.280
2.59810	4.45741	144.270
3.42064	5.86872	144.265
4.11855	7.06518	144.298
3.95958	6.79345	144.262
2.71834	4.66395	144.257
	Mean,	144.272

A slight correction for a little unseparated praseodymium raises the value to 144.275. This is doubtless the best determination of the constant yet made.

Erbium.—Hofmann,[1] by analyses and syntheses of the sulfate, has made three new determinations of the atomic weight of "neoerbium."

Weight Er_2O_3.	Weight sulfate.	Weight Er_2O_3.	At. wt. Er.
0.3117	0.5070	0.3117	167.67
0.4486	0.7296	0.44863	167.73
0.3718	0.6048	0.3718	167.64
		Mean,	167.68

The oxide in the first column was converted into sulfate, which, on calcination, gave the oxide of the third column. Calculated with S = 32.07.

The Helium-Argon Group.—Watson[2] has determined the weight of a normal liter of helium as 0.17814 and 0.17830 gram. Hence He = 3.994. For neon, eleven determinations of the normal liter ranged from 0.8997 to 0.9006 gram; in mean, 0.9002. This, by the method of limiting densities, gives Ne = 20.200. By the same method Watson[3] has reduced the densities of krypton and xenon, as measured in 1908 by Moore.[4] The final values are Kr = 82.92 and Xe = 130.22.

The density of argon has been redetermined by Fischer and Hähnel.[5]

[1] *Ber.*, 43, 2635.
[2] *J. Chem. Soc.*, 97, 810.
[3] *Ibid.*, 97, 833.
[4] *Proc. Chem. Soc.*, 24, 273.
[5] *Ber.*, 43, 1435.

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The mean of seven determinations is 19.945, referred to O = 16. Hence A = 39.89.

Ramsay and Gray,[1] by means of the microbalance, have been able to weigh the gaseous emanation of radium, for which they propose the name *niton*. The values thus found for its molecular weight are 222, 216, 227, 218, 217, in mean 220. The same value was also found by Debierne[2] by a different method.

Miscellaneous Notes.—Richards and Baxter[3] have investigated the subject of density corrections, or in other words the reduction of weights to a vacuum. They regard the validity of the corrections, as applied at Harvard, as well established. Relations between the atomic weights have been studied by Howard.[4] Dubreuil[5] has continued his recalculation of the determinations of Stas.

[Contributions from the Chemical Laboratory of Harvard College.]

THE ULTRAVIOLET ABSORPTION SPECTRUM OF AQUEOUS SOLUTIONS OF NEODYMIUM CHLORIDE.

By Gregory Paul Baxter and Truman Stephen Woodward.

Received December 22, 1910.

In a recent paper upon the atomic weight of neodymium[6] the absorption spectrum of aqueous solutions of neodymium salts from λ 7000 to λ 4000 is described. After the earlier measurements were made a large quartz spectrograph became available, and with this instrument the ultraviolet absorption spectrum of aqueous neodymium chloride has been examined.

The spectrograph was constructed by R. Fuess, Berlin. It has lenses 5 cm. in diameter, provided with diaphragms, and of about 80 cm. focal length, while the 60° Cornu prism is of 5 cm. base and 4.5 cm. high. In order to avoid as far as possible difficulty from double refraction the diameter of the lenses was diminished one-half with the diaphragms. By means of a series of trial negatives, with the spark of a cadmium alloy for illumination, the prism was set in the position of minimum deviation for approximately λ 3400, and the positions of the collimating and camera lenses were so adjusted that the region λ2500 to λ7500 was in fair focus throughout. Owing to the curvature of the spectrum image, it was not possible to have a wider range in focus at any one time. However, this range included the whole of the best continuous spectrum which we were able to produce.

[1] *Compt. rend.*, 151, 126.
[2] *Ibid.*, 150, 1740.
[3] This Journal, 32, 507.
[4] *Chem. News*, 101, 181, 265.
[5] *Bull. soc. chim.*, [4] 7, 119.
[6] Baxter and Chapin, *Proc. Am. Acad.*, 46, 215 (1910); This Journal, 33, 13.

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Comparative exposures with an incandescent Welsbach mantle, an acetylene flame, and a Nernst glower showed the last to be relatively richer in the shorter wave lengths, while the acetylene flame, although better in this respect than the Welsbach mantle, gives a slightly discontinuous spectrum in certain regions of short wave length. The foregoing experience is in accord with that of many previous investigators. All subsequent experiments were therefore carried out with the Nernst glower as the source of illumination. The light of the glower as well as that of the metallic spark used in the comparison spectra was condensed on the slit by means of a large quartz lens of 20 cm. focal length.

Measurements of wave length were made by comparison with the spectrum of an iron spark. The absorption spectrum and the iron spectrum were produced through adjoining portions of the slit by means of diaphragms. Since it was unnecessary to alter the position of the plate holder between the exposure of the plate to the absorption spectrum and to the iron spectrum, there was no possibility of error from lateral motion of the plate. The computation of wave lengths was made by means of a comparator and wave length curve, while the identification of the prominent iron lines was facilitated by comparison with a cadmium spectrum.

The neodymium chloride solution was contained in a tube of clear fused quartz 20 mm. in diameter placed close to the slit. Exposures of from one minute to one hour were made, first with a saturated solution of the salt, then with solutions of one-half, one-quarter and one-eighth the original concentration. Although the first two dilutions effected the resolution of the broad absorption band $\lambda 3450$–$\lambda 3580$ into four narrower ones, the third dilution produced no further effect of this sort. Since the absorption bands of the last solution were already faint, no further dilution was considered necessary.

The material examined was Fraction 2931, the purification of which has already been described in detail in the earlier paper upon the atomic weight of neodymium.[1] This specimen is one of those used in the measurements of the absorption spectrum of neodymium salts in the visible region. Previous examination has indicated that this fraction is very pure except for a trace, less than 0.05 per cent., of praseodymium salts. Since praseodymium salts have no narrow absorption bands in the ultraviolet region, no complications are introduced by this impurity. In preparing the chloride, the neodymium was precipitated as oxalate, the oxalate was ignited to carbonate and oxide, the product was dissolved in hydrochloric acid and the chloride was once crystallized from concentrated hydrochloric acid solution. Although the crystals were centrifugally drained, they undoubtedly retained a small amount of mother

[1] *Loc. cit.*, 221.

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liquor. Hence the solution of the chloride contained a slight excess of hydrochloric acid.

In the first column of the following table are given the wave lengths of the central portions of all the absorption bands observed either in concentrated or in dilute solutions. In each case the measurement was made in the most dilute solution in which the band was observed. The second column contains a description of the character of the bands. The remaining columns give the results obtained by other recent investigators. Of the latter, only Holmberg employed material of a high degree of purity.

Baxter and Woodward.		Holmberg.[1]	Uhler and Wood.[2]	Jones and Anderson.[3]
4327	weak, narrow	4330	433	4330
4290	very weak, narrow	....	..	4290
4274	very strong, narrow, sharp	4271	427·5	4275
4180	weak, narrow	4183	418	4180
3801	weak, very narrow	3802–3806	381	..
3556	strong, narrow	3555–3565	355	3560
3540	very strong, narrow	3530–3545	..	3540
3507	strong, narrow	3490–3510	350	3505
3465	very strong, narrow	3455–3480	347	3465
3399	weak, narrow	3410–3430	..	3390
3288	strong, very broad, diffuse	....	..	3225
3231	weak, narrow	....	..	..
3144	weak, broad, diffuse	....	..	..
3067	very weak, narrow	....	..	..
3047	very weak, narrow	....	..	..
3030	very weak, narrow	....	..	..
3015	very weak, narrow	....	..	..
2998	medium, narrow	....	..	..
2983	strong, narrow, sharp	....	..	2985 double
2937	very weak, diffuse	....	..	..
2913	medium, narrow	....	..	..
2902	medium, narrow	....	..	2900

The comparator could be read with certainty to 0.05 mm. while this quantity corresponded to one unit in the fourth figure of the wave length at $\lambda 3700$. Still, since it is difficult to be sure of the exact position of the center of even a narrow absorption band, some uncertainty undoubtedly exists in the fourth figure of our results. The numerical agreement of our figures with those of the other experimenters is very satisfactory.

It is worth noting that all the bands previously observed by others were found in the spectrum of our preparation, while the bands which we observed and which are lacking in the older results are in most cases so weak that they can be observed only under the most favorable conditions.

[1] *Z. anorg. Chem.*, 53, 113 (1907).
[2] "Atlas of Absorption Spectra," *Pub. Car. Insi.*, 71, 54 (1907).
[3] "Absorption Spectra of Solutions," *Ibid.*, 110, 76 (1909).

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.][1]

ORGANIC AMALGAMS: SUBSTANCES WITH METALLIC PROPERTIES COMPOSED IN PART OF NON-METALLIC ELEMENTS.[2]

BY HERBERT N. MCCOY AND WILLIAM C. MOORE.

Received November 30, 1910.

A. Introduction.

During the last two decades a vast amount of experimental evidence has been accumulating that electricity is granular in structure, though such a conclusion was strongly indicated three-quarters of a century ago by Faraday's discovery of the facts epitomized in the law of electrochemical equivalents, as first pointed out by Helmholtz in 1881. The ultimate granules of electricity are the electrons. The charge of the electron is negative in sign. In fact we have decisive experimental evidence of only this one kind of free electricity, positive electrification of a body being from this standpoint merely a deficiency of electrons.

J. J. Thomson[3] has shown how, from the conception of an atom made up of electrons rotating in a sphere of positive electrification, there follows a simple explanation of many of the properties of an atom, including valence: a univalent atom, if negative, being one that can gain an electron, if positive, one that can lose an electron. A bivalent atom can gain or lose two electrons, a trivalent atom three, etc. According to this hypothesis, the most fundamental property of an atom is this tendency to gain or lose one or more electrons. The tendency to lose electrons is greatest for the alkali metals and least for the noble metals. The tendency to gain electrons is small for sulfur and great for the halogens, the maximum being reached in fluorine. According to this view, for example, sodium and chlorine react with great energy because of the great tendency for each atom of free sodium to lose an electron, on the one hand, and each atom of free chlorine to take up an electron, on the other. The action consists, therefore, in the transfer of an electron from an atom of sodium to an atom of chlorine.[4] The components of the molecules of solid salt are therefore not an *atom* each of sodium and chlorine, but an *ion* of sodium combined with an *ion* of chlorine, if by the term *ion* we now mean an atom ± an electron. The more or less complete "electrolytic dissociation" or "ionization" which occurs upon dissolving a salt in water is then due to the marked lessening of the electric force which holds

[1] The final part of the experimental work of this investigation was carried out at Columbia University after my removal from Chicago to Columbia. I wish here to make acknowledgment of the many courtesies shown me by several of my colleagues in the Havemeyer Laboratories. William C. Moore.

[2] Preliminary report read at the Detroit Meeting of the American Chemical Society, June, 1909. *Science*, 30, 315 (1909).

[3] *Phil. Mag.*, 1, 237 (1904).

[4] Thomson, "The Corpuscular Theory of Matter," p. 120, New York, 1907.

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together the ions of the solid salt by reason of the very great dielectric constant of water.[1]

The application of the electron theory to the metallic state by Riecke, Drude, Lorentz, Thomson and others has led to results of the highest significance. Though the details of the relations of the electrons to the atoms are viewed somewhat differently by various physicists it is however agreed by those who are working in this field that metals owe their most characteristic metallic properties of a *physical* nature, to the *mobil* or free electrons which they contain. The absence of metallic properties in the solid non-metallic elements is, by this hypothesis, due to the supposed tendency of the atoms of such elements to *gain*, not lose, electrons, for which reason such a non-metallic solid will contain very few free or mobil electrons.

Thus according to one view, the electrons, which are perhaps as numerous as the atoms of the metal, move about freely among the atoms, with which they are considered to be in kinetic equilibrium. Electric conductivity is then due to the drift of these electrons under the influence of the potential in the wire. Thermal conductivity of metals is explained equally satisfactorily by the electron hypothesis. The calculated ratio of thermal to electrical conductivity and also the temperature coefficient of the ratio are in good agreement with the facts. Other metallic properties, including opacity to light, reflecting and radiating power, the Hall effect, the Thomson effect, the Peltier effect, etc., are equally well accounted for.

The most characteristic *chemical* property of a metal is its ability to form the positive ions of salts. Every true metal has this property well developed. If we electrolyze a solution of a salt, say silver nitrate, the free positive ions of silver are attracted and move toward the negative electrode, on coming in contact with which the ion has forced into it an electron, which converts it into an atom of silver. The aggregation of such atoms has metallic properties owing to the great tendency of each atom to give up an electron.

While the atom of any true metal can by loss of one or more electrons form the + ion of a salt, there are of course large numbers of salts, mostly organic, whose + ions are not the residues of metallic atoms. These salts have most of the properties characteristic of salts derived from true metals but are distinguished from the latter by the fact that they are the derivatives of the "compound radicals." When we consider, theoretically, the behavior upon electrolysis of a salt of a base-forming compound radical it is difficult to see wherein the result should differ from that obtained with a salt of a metallic element. In this case, as in the other, positive ions are attracted to the cathode and upon striking it can

[1] Thomson, *Phil. Mag.*, 36, 320 (1893); Nernst, *Z. physik. Chem.*, 3, 531 (1894).

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gain electrons. If the electron theory of the metallic state is as fundamental as it seems to be, there would be little reason to doubt that the aggregate of such free radicals would be a body having metallic properties; for such a hypothetical body would be made up of radicals which, analogous to metallic atoms, could easily lose electrons. The mass would then contain an abundance of mobil or free electrons and in such case would possess high electrical and thermal conductivity, metallic luster, etc. Practically, however, several causes may prevent the isolation of such metallic substances. We know that it is not possible to separate by electrolysis many metals from aqueous solutions of their salts. This is the case with sodium, whose electric solution tension exceeds that of hydrogen by so much that the latter element is liberated from the water by the current and no sodium is obtained on the electrode. Similar relations may obtain in the electrolysis of an organic salt, as is shown in the experimental part. On the other hand, it is theoretically possible that such a compound metal may be so unstable in the free state that it suffers spontaneous decomposition at the moment of its formation from its ions. A third possibility is exemplified by the case of hydrogen. For a long time it was thought by some chemists that hydrogen in the solid form would have metallic properties, since acids may be considered "hydrogen salts." The fact that solid hydrogen is now known to have no metallic properties[1] proves clearly the fallacy of the old idea and seems also to be a flat contradiction of our hypothesis. Now hydrogen differs from the metals in one other important respect: while the molecules of metallic vapors are always monatomic those of hydrogen are diatomic. Thomson has considered the question of the theory of the union of two like atoms to form a molecule of an elementary gas, and has shown very convincingly that it is reasonable to conclude that one atom sends its valence electron into the other and that the combination is entirely analogous to that when two unlike atoms combine. If this is the case it is possible to understand why solid hydrogen has no metallic properties: its valence electrons are bound and not *free* or *mobil*. It is possible that some positive organic ions will behave like hydrogen when set free and unite in pairs to form double radicals. These would not be expected to have metallic properties, the valence electrons being bound. Turning now from theory to facts, we find that there is already considerable evidence that free electropositive radicals have metallic properties. The case of ammonium amalgam is familiar to every chemist. This remarkable substance was discovered by Seebeck[2] and practically

[1] In some cases however hydrogen seems to have some properties of a metallic character: it dissolves readily in palladium and, when nascent, diffuses easily through iron. Bellati and Lussana, *Z. physik. Chem.*, 7, 229 (1891).

[2] *Ann. chim.*, 66, 191 (1808).

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simultaneously by Berzelius and Pontin. Davy[1] compared ammonium amalgam with the amalgams of sodium and potassium and was led to announce his famous ammonium hypothesis: the radical ammonium was analogous to the alkali metals and was said to exist in metallic form, united with mercury, in the amalgam. Berzelius and Ampere also supported this view. On the other hand Gay-Lussac and Thenard[2] concluded that the so-called amalgam is only a mixture of ammonia, hydrogen and mercury, a view shared by many others, among them Seely,[3] who found the volume of the inflated mass to be inversely proportional to the pressure upon it. The case against the metallic ammonium hypothesis was made still stronger by the evidence furnished by Landolt[4] who was unable to precipitate from solutions of their salts either copper or silver by means of ammonium amalgam.

The first really convincing evidence in favor of the ammonium hypothesis was furnished by LeBlanc[5] who electrolyzed a solution of an ammonium salt with a mercury cathode. The apparatus was so arranged that simultaneous measurements of the polarization potential could also be made. This potential rose in a few minutes to a maximum which was nearly as great as that given by a sodium salt. The really important result, however, was observed after the polarizing current was cut off. The mercury cathode, which showed the inflation characteristic of ammonium amalgam, was still strongly electronegative toward the solution and remained so for 10–20 minutes. This effect was not due to hydrogen, it having been shown that the hydrogen polarization potential was considerably smaller and that it fell off almost as soon as the current was interrupted. Coehn[6] next showed that the failure of Landolt's experiment was due to too high a temperature. Ammonium amalgam prepared at 0° would precipitate copper from the sulfate without difficulty. This result was of itself insufficient to prove the metallic nature of ammonium, since free hydrogen was always present in the amalgam and may have been the active substance in the reaction. To remove any doubt Coehn then showed that not only are cadmium and zinc precipitated by the cold amalgam but that barium amalgam results from the action, at zero, of ammonium amalgam on a solution of barium chloride. This fact was independently discovered later by G. M. Smith,[7] who also obtained sodium and potassium amalgam in a similar manner. Thus the experiments of LeBlanc, Coehn and G. M. Smith furnish in-

[1] *Phil. Trans.*, 1810, 37.
[2] See Routledge, *Chem. News*, 26, 210 (1872).
[3] *Chem. News*, 21, 265.
[4] *Ann. Chem.*, 6, 346 (1868).
[5] *Z. physik. Chem.*, 5, 467 (1890).
[6] *Z. anorg. Chem.*, 25, 430 (1900).
[7] THIS JOURNAL. 29, 844 (1907).

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disputable evidence of the metallic nature of ammonium in ammonium amalgam. LeBlanc's polarization experiments also included the study of the salts of a number of substituted ammonias. Mono-, di- and tetramethyl and monoethyl ammonium ions gave results more or less like those shown by ammonium, from which facts LeBlanc concluded that in these cases also amalgams were formed, although none of the supposed amalgams were isolated.

In the present investigation we have isolated two of these organic amalgams and have demonstrated beyond question their metallic nature and have thereby furnished additional evidence of the possibility of the preparation of substances with metallic properties composed in part of non-metallic elements.

B. Preparation of Tetramethyl Ammonium Amalgam.

The first attempts at the preparation of tetramethyl ammonium amalgam were made by the action at 0° of 8 per cent. sodium amalgam on a 25 per cent. aqueous solution of tetramethyl ammonium chloride. Hydrogen was given off, but no new product resulted. The electrolysis of aqueous solutions of the chloride under various conditions of temperature and concentration gave always colloidal mercury at the mercury cathode, but no amalgam could be isolated. It was thought that an amalgam might be formed by the action of the current and be rapidly decomposed by the water. Accordingly, absolute alcohol was substituted for water as solvent and proved wholly satisfactory.

The first successful preparation of tetramethyl ammonium amalgam was accomplished by the electrolysis of a saturated solution of tetramethyl ammonium chloride in absolute alcohol, using a platinum anode and a mercury cathode. The temperature was —10°. By means of a potential-reducing device, the direct current of the lighting circuit (110 volts) was cut down to 18 volts, and the current was allowed to run at this pressure for thirty minutes. As prepared in this way, the amalgam is a stiff mixture of shining crystals of the amalgam and the excess of mercury; it is but very slightly inflated,[1] silvery white in color and decidedly metallic in appearance. In contact with alcohol it is moderately stable, but reacts violently with water.

Since this first preparation was made, the amalgam has been prepared by this method many times and many of its properties studied. However, since in using a platinum anode chlorine is evolved, the method has been improved by the substitution of an anode of silver-plated platinum gauze.

In the most convenient form of apparatus for the production of the

[1] When properly prepared, it shows at temperatures below +10° absolutely no tendency to become inflated, in which respect it differs markedly from ammonium amalgam.

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amalgam, a small Gooch funnel is used as the electrolytic chamber. This is supported by passing the stem through a one-hole rubber stopper closing the tubulure of an inverted four-liter bell jar, which serves as an ice chamber. The whole apparatus is supported at an appropriate height, by means of a ring and a universal clamp, on an iron stand. A piece of rubber tubing fastened to the stem of the Gooch funnel, and closed by a pinchcock, affords a convenient outlet for the amalgam after it is formed. The anode consists of a piece of silver-plated platinum gauze rolled into cylindrical form. This gauze is welded to a stout platinum wire which passes between the edge of the funnel and the rubber stopper closing the funnel. The negative wire, insulated by a glass capillary tube, enters the funnel through one leg of a T tube. The upper end of this T tube, where the wire enters, is closed by means of universal wax or a glass cap and a piece of rubber tubing, while a calcium chloride tube is attached to the other leg of the T to exclude moisture. A thistle tube, reaching almost to the mercury cathode, is inserted into the second hole in the rubber stopper, and serves for the introduction of mercury or of the electrolyte.

Fitted up in this manner, the procedure for making a "run" with the apparatus is as follows: The mercury to serve as a cathode is run into the electrolysis chamber through the thistle tube; the solution of the electrolyte is then introduced, the bell jar having previously been filled nearly to the top of the Gooch funnel with crushed ice or a freezing mixture. The current is then turned on, the potential and strength being regulated so that about 0.25 ampere passes through the cell, under ordinary circumstances. After running for 10–15 minutes, the current is interrupted; the excess of mercury run off through the delivery tube at the bottom of the apparatus, into a dry dish; the amalgam is then run off into a second dry dish and used as desired, while the excess of mercury is poured, through the thistle tube, back into the electrolytic cell. In this way a number of successive runs can be made with but little interruption.

C. Properties of Tetramethyl Ammonium Amalgam.

Physical Properties.—As prepared above, at temperatures of from —10 to —5° the amalgam is a pasty, *crystallin* mass about the color of metallic zinc. While at 0° or at temperatures slightly above 0° the crystallin structure is not so pronounced, yet on several occasions almost solid lumps have been observed in the amalgam formed at 0°. It is somewhat lighter than mercury, as it always floats on the latter. There is evidence that more than one active phase exists in the amalgam. The surface tension of the amalgam is less than that of mercury. There is little tendency, from —10 to 0°, toward inflation of the amalgam, but when the temperature of a sample, washed with absolute alcohol and

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partially dried with filter paper, was allowed to rise slowly, the volume increased and at 25° was about twice the volume at 0°.

Stability of the Amalgam.—When the temperature of the clean amalgam is kept near 0° it is quite stable, but on allowing the temperature to rise it decomposes very rapidly. Trimethylamine is one of the products of this decomposition, as is shown by the powerful fish-like odor. The other products have not been fully investigated; it is hoped to make a further study of this point.

General Chemical Properties.—If the amalgam is run from the electrolytic cell directly into a clean, dry flask, it becomes covered with a gray-white crust, probably tetramethyl ammonium hydroxide, as it reacts with water to form an intensely alkaline solution.

The Reaction of Water on the Amalgam.—When allowed to come in contact with water a violent action takes place; hydrogen is formed and the whole of the mixture becomes ink-black, rapidly turning gray, and a gray, colloidal solution is the final result. Le Blanc[1] probably got the same substance by the electrolysis of aqueous solutions of tetramethyl ammonium chloride, using a mercury cathode—a result we have also obtained under similar conditions. We studied the phenomenon further as follows.

The amalgam was formed as usual, in the apparatus described above. After the current had been allowed to run for some time, the excess of mercury was drawn off into a clean, dry dish. The amalgam was then drawn off into a second small porcelain dish, quickly washed several times with absolute alcohol, dried with filter paper, and the dish held in the hand, against the inside edge of a 600 cc. beaker. A fine stream of water was now forcibly directed against the upper surface of the amalgam, near the lip of the dish, in such a way that the colloidal black deposit was swept into the beaker without carrying along globules of mercury. The washing with water was continued until little or no further action between the amalgam and the water was noticed. When the main portion of the "black deposit" had been swept into the beaker, in nearly every case a black, nearly solid residue, small in amount, was noticed floating on the globule of mercury left. This black substance acted less vigorously with water than the pasty amalgam, but still gave a "colloidal black deposit" with water. An explanation of this fact will be taken up later. The above outlined process was repeated a number of times, until sufficient material had been accumulated; the black residue was then filtered off through a weighed Gooch crucible, dried at 108–110° and weighed; the filtrate was reserved for further experimentation. This weighed residue was then dissolved in hot nitric acid, repeatedly evaporated with concentrated hydrochloric acid until nitric acid was

[1] Le Blanc, *loc. cit.*

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practically completely eliminated, then diluted, filtered free from asbestos fibers, and the mercury precipitated by hydrogen sulfide. This precipitate was washed, dried, washed several times with carbon disulfide, dried at 108–110° and weighed. In three analyses in which from 0.4 to 0.8 g. of substance was taken the percentages of mercury found were 98.06, 97.93, 96.98.

These low but consistent values of the mercury content of the black deposit mean that the substance is in all probability the pure element, the low values being due either to (1) water absorbed to a slight degree, or (2) to a little occluded hydrogen. Less plausible would be the assumption that (1) the deposit is a mixture of mercury and mercurous oxide, or (2) that it is a compound containing the tetramethyl ammonium radical. The deposit after drying generally aggregated into actual globules, and the portion which did not do so became silvery white in color; this disposes of the first assumption, and there is no other evidence in favor of the second. The mercury itself, used in the preparation of the particular amalgams from which the black deposit was obtained for analysis, was, by analysis, 99.86 per cent. pure. The nature of the impurity was not determined.

The filtrates from each of the above experiments and a number of others were titrated with standard hydrochloric acid; the results were calculated to $N(CH_3)_4$ and the ratio, $N(CH_3)_4$ to Hg, was determined from these results, and from the weight of the colloidal mercury. In the table below, in the experiments in which the values "calculated weight, $N(CH_3)_4Cl$" and "actual weight, $N(CH_3)_4Cl$" are given, the solutions after titration were actually evaporated to dryness, and the residues weighed. These residues were then combined, purified and analyzed as shown below.

TABLE I.

Expt. No.	Cc. 0.1 *N* HCl.	98% Wt. colloidal Hg.	$N(CH_3)_4$ calc.	A.	Wt. res.	Calc. wt. $N(CH_3)_4Cl$.
270	4.00	0.1329	0.0297	1.66	...	...
271	2.50	0.0515	0.0186	1.02	...	...
272	9.50	0.2303	0.0705	1.21	...	...
273	5.82	0.4496	0.0431	3.87	...	...
274	12.72	0.2797	0.0943	1.10	...	...
277	7.12	0.3037	0.0527	2.13	...	...
279	18.18	0.3629	0.1348	0.99	0.230	0.199
282	11.11	0.7946	0.0823	3.57	...	...
283	15.43	1.3451	0.1143	4.35	0.180	0.169
285	26.17	0.3713	0.1938	0.71	0.294	0.286
288	12.28	0.4161	0.0910	1.69	0.126	0.134
291	35.50	0.4607	0.2630	0.60	0.395	0.389
292	23.71	0.4983	0.1757	1.05	0.252	0.260

In the column headed "A" is given the number of atoms of colloidal mercury formed for each tetramethyl ammonium ion set free. It is

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seen that this ratio is not constant. Four of the thirteen values, however, are close to *unity*, which may indicate a possible compound of the formula $HgN(CH_3)_4$. Since the colloid analyzed to 98 per cent. mercury, this per cent. of the *actual* weight of the colloid is used in the calculations.

In several of the experiments in which the colloidal mercury was not used for analysis, it was weighed on dried filter papers. In some cases the deposit was coagulated by the addition of sodium chloride and in others by the addition of concentrated hydrochloric acid. The latter, however, was abandoned as a coagulant since it dissolved some of the deposit, though not much. In experiments 270, 271, 272, 273, phenolphthalein was the indicator used, while in the rest of the experiments methyl orange was used.

The values in column "A" are to be taken as approximate only, as it was always difficult to remove every trace of the colloid from the small dish to the beaker by means of wash water. Again, there was always a slight decomposition of the amalgam not due to the action of water.

As stated above, the residues of supposed tetramethyl ammonium chloride left on evaporating to dryness the solutions in experiments 279, 283, 285, 288, 291 and 292 were combined and analyzed. This analysis was made as follows: The combined residues were dissolved in water, the solution evaporated to dryness, the resulting mass taken up with absolute alcohol and precipitated with ether. From the mother liquor of this ethereal solution, a second crop of crystals was obtained and this was recrystallized from absolute ethyl alcohol. These samples were dried, and weighed portions dissolved in water and titrated with decinormal silver nitrate, using potassium chromate as indicator. 0.1290 g. of salt of first crystallization required 11.82 cc. of 0.1 *N* $AgNO_3$; 0.1044 g. of salt of second crystallization required 9.55 cc. 0.1 *N* $AgNO_3$. Per cent. Cl calculated for $N(CH_3)_4Cl$, 32.36. Found: I, 32.27; II, 32.47. The results of these two analyses, with the close agreement between the actual and calculated weights of $N(CH_3)_4Cl$, show conclusively that the amalgam contains the tetramethyl ammonium group.

Two analyses of the gas evolved when the amalgam reacts with water were made as follows: A quantity of the amalgam was run out into a small dish and quickly washed with absolute alcohol and dried as much as possible by means of filter paper. It was then decomposed by water and the gas evolved collected. This process was repeated until an amount of gas sufficient for analysis was obtained. The gas was then transferred to a eudiometer filled with mercury, measured, mixed with air, measured, exploded, and the contraction noted. Concentrated sodium hydroxide was now admitted to the tube, but no contraction resulted, hence no carbon dioxide was formed on explosion. In the first analysis

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11.00 cc. of the unknown gas were used, and the contraction of the mixture on explosion was 15.30 cc., equivalent to 92.73 per cent. of hydrogen; while in the second case 6.50 cc. was the contraction when 4.6 cc. of the unknown gas were used, indicating 94.13 per cent. of hydrogen present.

These experiments should be regarded as qualitative only; no corrections were made for the vapor pressure of water; the experiments were made simply to demonstrate that hydrogen is the gas evolved when the amalgam is treated with water, and that no gas containing carbon was produced.

Reaction of the Amalgam with Aqueous Solutions of Various Salts.—A cold concentrated solution of ammonium chloride was treated with tetramethyl ammonium amalgam. Ammonium amalgam, as shown by the inflation peculiar to this substance, was formed. *There were absolutely no indications of colloidal mercury.* Part of the same tetramethyl ammonium amalgam reacted in the usual way with water. A saturated solution of potassium chloride was treated with tetramethyl ammonium amalgam at room temperature. There was only a trace of colloidal mercury formed. After the mixture had stood for three minutes, the residual mercury was washed quickly six or seven times with water and then allowed to stand in contact with water. There was absolutely no indication of the presence of tetramethyl ammonium amalgam, but there was a slow reaction between the mercury and the water, gas being evolved. That potassium amalgam had been formed was proved by acidifying the aqueous solution with hydrochloric acid, adding a few drops of chloroplatinic acid and evaporating to dryness; the residue, when treated with water, remained for the most part undissolved; the yellow crystals were undoubtedly potassium chloroplatinate. A solution of sodium chloride, approximately three times normal strength, was treated with tetramethyl ammonium amalgam. No colloidal mercury was formed, but a quiet action ensued between the solution and the amalgam. This was allowed to continue for four minutes, then the mercury was quickly washed twelve times with cold water and covered with water. Gas was evolved for more than two hours. The resulting solution was alkaline to litmus—conclusive proof that sodium had replaced the tetramethyl ammonium group in the amalgam. Concentrated solutions of cesium and rubidium chlorides in water and thrice normal potassium chloride were each treated with parts of the same lot of tetramethyl ammonium amalgam. With the cesium chloride, violent action occurred with the formation of colloidal mercury, but the action was less violent than when pure water alone is used. With the rubidium chloride, only a little colloidal mercury was formed, and with the potassium chloride, none at all. When the experiment was repeated, using normal solutions of each salt in water, the results were in the same order, the only difference being

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that with potassium chloride a little colloidal mercury was formed, less, however, than with rubidium chloride.

An aqueous solution of copper sulfate of unknown concentration was treated with tetramethyl ammonium amalgam. The action was fairly violent; only a little colloidal mercury was formed. There was effervescence, and after standing fifteen minutes, the mercury was covered with bubbles of gas. At this stage, very thin, copper-red crystals were noticed floating on the surface of the supernatant liquid. The mercury itself had a coppery color. It was washed seven or eight times with water, and showed every indication of the presence of copper amalgam. Part of it was dissolved in nitric acid, the resulting solution evaporated and ammonium hydroxide added to the *greenish* residue. The characteristic blue color of the cupri-ammonium ion was seen while some of the original mercury from which the amalgam had been formed gave absolutely no indications of the presence of copper on similar treatment.

Mercuric chloride in aqueous solutions was also treated with tetramethyl ammonium amalgam; the reduction to the mercurous state was more rapid than when pure mercury acts on mercuric chloride. Colloidal mercury was formed. The flocculent gray precipitate was filtered off and tested with ammonium hydroxide; the characteristic black color which this reagent affords with mercurous chloride was produced.

Normal aqueous hydrochloric acid acts vigorously on tetramethyl ammonium amalgam, only a little colloid, however, being formed. We have also shown[1] that the amalgam precipitates copper and zinc from alcoholic solutions of their nitrates. All these experiments go to show the complete analogy between the tetramethyl ammonium radical and an ordinary alkali metal, and will be referred to again after the consideration of further experimental work.

The Action of Alcohol on the Amalgam.—One of the first properties of the amalgam to be studied was the reaction with alcohol. The speed of this reaction was determined, approximately, at 0°, as follows: The amalgam was made in the usual way; it was washed four times with absolute alcohol and then immediately poured into absolute alcohol in a conductivity cell at 0°. The resistance of the solution was determined at definit intervals and from the values for this resistance at the various times the speed of the reaction was calculated, applying the formula for a unimolecular reaction, $k = 1/t \log_e a/(a - x)$. The mixture was, of course, stirred to insure uniformity of concentration as far as possible. If W is the resistance at the time t, and W_a is the final resistance, it is easy to show that $k = 1/t \log_e W(W - W_a)$, since the initial resistance, that of pure alcohol, is very high. Using this formula, k, the rate of for-

[1] McCoy and Moore, *Science*, 30, 315 (Sept. 3, 1909).

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mation of the tetramethyl ammonium ion when the amalgam is in contact with absolute ethyl alcohol is calculated from the results below:

TABLE II.

Experiment No. 33.			Experiment No. 35.		
Time, t (minutes).	Resistance (ohms) W.	k.	Time, t (minutes).	Resistance (ohms) W.	k.
0	61,600	..	0	15,400	..
11.5	840	0.0238	3	399	0.1136
21.5	308	0.0492	6	300	0.0708
31.5	264	0.0456	9	250	0.0686
41.5	234	0.0472	12	215	0.0648
51.5	205	0.0752	16	194	0.0563
61.5	201	..	19	173	0.0577
71.5	201	..	24	150	0.0609
81.5	201	..	29	139	0.0606
..	...	..	34	129	0.0646
..	...	..	40	117	0.0833
..	...	..	83	115	..
..	...	..	100	115	..

D. The Electrode Potential of the Electrode: Tetramethyl Ammonium Amalgam, Half-normal Tetramethyl Ammonium Chloride in Absolute Alcohol, and in Water.

The electromotive force of the electrode: tetramethyl ammonium amalgam, 0.5 N $N(CH_3)_4Cl$ in absolute alcohol, was measured, at 0°, against a decinormal calomel electrode. Measurements were made by a compensation method and were carried out both while the primary or polarizing current was running and after the amalgam had been formed and the polarizing current was cut off.

In order to make the measurements while the polarizing current was running, it was necessary very rapidly to shift the connections of the amalgam electrode from the polarizing circuit on the one hand to the measuring circuit on the other. Le Blanc[1] used for this purpose an electric tuning fork, but in the present work a remodeled electric bell gave better results as a vibrator. The gong and clapper were removed, and a platinum contact point passed through the clapper stem, so that when the armature of the bell was in motion it made contacts in such a way that the amalgam electrode was alternately in connection with the polarizing circuit and the measuring circuit. When the vibrator was at rest, permanent connection was made between the amalgam electrode and the measuring circuit.

Since the electrode potential of the amalgam was measured against a decinormal calomel electrode, both while the polarizing current was running and after it was cut off, provision had to be made for the anode of the polarizing circuit. This anode was made of silver wire, and was

[1] Le Blanc, *loc. cit.*

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run between the stopper and the edge of the glass half-cell serving as container for the mercury forming the cathode. Connection between this mercury and the negative terminal of the polarizing circuit (through the circuit shifter) was made by means of a platinum wire sealed into a glass capillary filled with mercury. This capillary passed through a hole in the rubber stopper. The glass half-cells containing the amalgam and calomel electrodes were immersed in crushed ice, while the capillary portions of the cells extended over the edge of the ice bath into the "bridge" solution of decinormal potassium chloride. The mercury used in the preparation of the decinormal calomel electrode, and as a cathode in the amalgam cell, was recently purified by distillation in a vacuum. A D'Arsonval galvanometer was used in the measuring circuit. In all instances the "zero" method of measurement was used.

The compensating current in the measuring circuit was derived from two storage cells; the polarizing current was taken from the lighting circuit of the laboratory and by means of a variable resistance in parallel with the electrolytic apparatus the voltage was regulated without difficulty.

TABLE III.—ELECTROMOTIVE FORCE OF THE AMALGAM-CALOMEL ELECTRODE CELL, AT 0°.

A. Polarizing current *on*.				B. Polarizing current *off*.			
Expt. No.: Time. Mins.	205. E. M. F. volts.	206. E. M. F. volts.	209. E. M. F. volts.	Expt. No.: Time. Mins.	205. E. M. F. volts.	206. E. M. F. volts.	209. E. M. F. volts.
0	0.229	0.240	0.247	0	2.6111	2.990	2.630
8	...	2.928	...	1.5	2.628	...	2.622
10	...	2.908	2.681	2	...	2.671	2.618
11	...	...	2.664	4	2.629	2.648	2.618
12	2.807	2.908	2.664	6	2.628	2.621	2.618
13	...	...	2.681	8	...	2.605	2.617
14	...	2.97	...	9	2.624	...	2.622
15	2.807	...	...	10	...	...	2.617
16	...	2.96	...	12	...	1.984	2.617
18	2.626	...	...	14	...	1.948	...
19	...	3.034	2.502	15	...	...	2.615
21	2.611	...	...	19	...	1.062	...
22	...	3.034	...	20	2.017	...	...
24	2.611	...	...	22	...	...	2.604
25	...	2.990	...	25	1.958	0.477	...
27	2.611	2.990	...	26	...	...	2.041
28	...	...	2.630	30	...	...	2.031
29	...	...	2.630	36	...	...	2.031
30	...	...	2.630	37	0.503	...	...
..	...	...	...	47	...	...	2.001

In making a measurement, the electromotive force of the two storage cells was first balanced against that of a cadmium cell. The polarizing current was then allowed to flow continuously through the half-cell in

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which the amalgam was to be formed, for several minutes. The connections having in the meanwhile been changed from the cadmium cell to the amalgam calomel electrode cell, the electric vibrator was set in motion, and the e. m. f. of the cell: Amalgam, 0.5 *N* $N(CH_3)_4Cl$ in absolute alcohol, 0.1 *N* KCl, 0.1 *N* calomel electrode, balanced against that of the two storage cells at intervals. After making measurements in this way for some minutes, the primary or polarizing circuit was broken, and the e. m. f. of the cell again measured at intervals. After completing this set of measurements, the current of the storage cells was again balanced against that of the cadmium element and the average of the two values of the electromotive force of the storage cells used in calculating the electromotive force of the amalgam calomel electrode cell. These two values of the electromotive force of the storage cell were always close together. The detailed results of these experiments are given in Table III.

In the series of values given when the polarizing current was cut off, the value for zero time is taken as the same as the final value obtained just before the polarizing current was cut off.

In addition to the potential measurements above, the potential of an amalgam cell using water as the solvent for tetramethyl ammonium chloride, of half-normal concentration, was determined. This set of

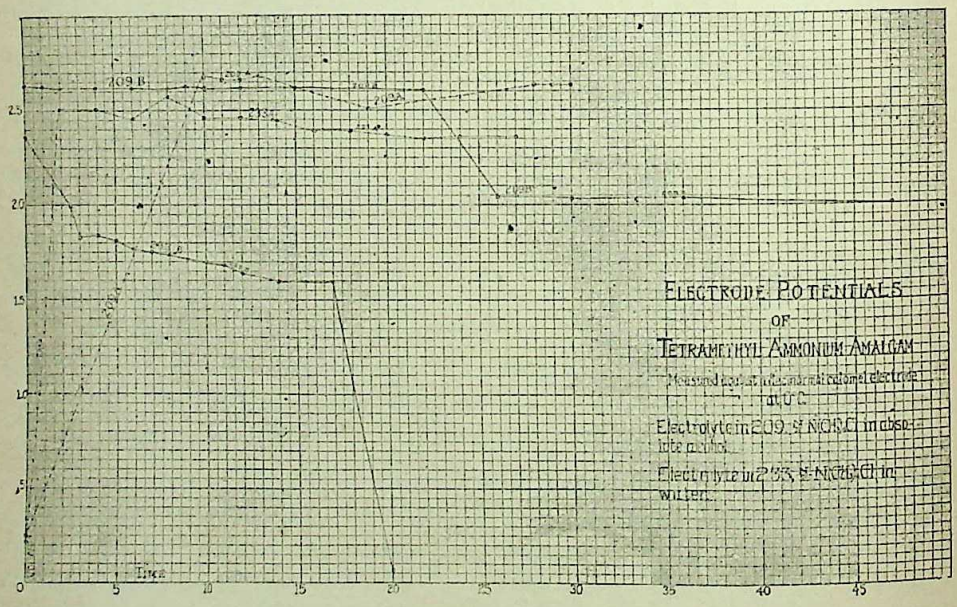


Fig. 1.

measurements was likewise made against a decinormal calomel electrode, at zero, in a manner exactly similar to that above. The results of this experiment, with the polarizing current on (Series A) and off (Series B) are given below:

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TABLE IV.

Time, min.....	0	2	2.5	4	6	8	10	12	14
Series A.....	0.219	2.507	...	2.507	2.452	2.571	2.46	2.46	2.448
Time, min.....	0	2.5	3	4	5	6	7	8	9
Series B.....	2.359	1.99	1.831	1.844	1.811	1.763	1.752	1.736	1.714
Time, min.....	16	18	20	22	24–27	...	...	...	...
Series A.....	2.387	2.387	2.373	2.352	2.359	...	...	...	...
Time, min.....	10	11	12	14	17	19	...	...	...
Series B.....	1.699	1.678	1.637	1.596	1.591	0.063	...	...	...

The curves for two experiments, Nos. 209 and 233, the one in which alcohol was the solvent, and the other, in which water was the solvent, are shown in Fig. 1.

E. Discussion of the Potential Measurements.

On examining the two curves, it is seen that their forms are very interesting. In 209 B, where the electrolyte was half-normal tetramethyl ammonium chloride, in absolute alcohol, the potential remained constant for some time after the polarizing current was interrupted. This constant value was about 2.62 volts; after awhile, however, the potential dropped rapidly to a new value near 2.00 volts.

In 233 B, with water as the solvent for the half-normal tetramethyl ammonium chloride, the average value of the potential, while the current was on, was about 2.4 volts, but on cutting off the polarizing current the potential dropped to about 2.0 volts immediately, then gradually fell to 1.6 volts, and in the end quickly dropped to almost zero.

The horizontal or nearly horizontal portions of these curves can have but one interpretation; a definit phase of the amalgam gives rise to a definit potential; and when this particular phase is exhausted, if there is a different phase possible, the potential drops to that of the new phase. Hence, in 209 (as in 205 and 206, as will be seen by plotting curves for these experiments) there were formed at least two phases: one may be the decomposition product of the other, or they may be coincident in the amalgam, the more active disappearing first.

Now, Wilsmore and Johnson[1] have recently shown that for the electrode potential of metal, using as a solvent, for the salt of the metal, liquid ammonia at —35.5°, a higher value is obtained than when water is the solvent. They account for this fact on the assumption that the degree of ionization is less in liquid ammonia than in water solutions of equivalent concentrations. This explains why, in the present instance, the electrode potential of one of the phases stable in contact with absolute alcohol solutions of tetramethyl ammonium chloride is 2.6 volts, while in contact with an aqueous solution of the same salt in equivalent

[1] Wilsmore and Johnson, *Elektrochem. Z.*, 14, 203.

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concentration the potential averaged about 2.40 volts. The two values, 2.6 volts in alcoholic solution and 2.4 volts in aqueous solutions of tetramethyl ammonium chloride, are obviously due then to the same phase, but when the polarizing current is cut off where water is the solvent the potential immediately falls because this phase is very reactive towards water. Likewise, the phase showing a potential of 2.0 volts in experiment 209 must be the same which shows a potential of 1.74 volts (average) in experiment 233, but this phase is likewise less stable in contact with water than alcohol as is shown by the slowly but constantly changing values in 233 B.

The high polarization values in experiments 205 and 206 are probably due to a still more active phase which did not appear in experiment 209.

These experiments do not afford the only proof at hand that more than one phase of the amalgam is formed. Throughout this work it has been noticed that immediately under the anode the amalgam formed has a more solid, more crystallin appearance and a darker color than the rest of the amalgam; in experiment 300, a portion of amalgam practically solid was formed. Again, when the amalgam is treated with water the first action is violent and the whole of the reaction mixture becomes inky-black, quickly turning to the gray color of ordinary colloidal mercury. On treating the amalgam with water in a flat dish and washing away the colloid by means of a stream of water as fast as it is formed a darker, more solid phase, floating on the mercury, has been noticed. While this phase still reacts with water to form the colloidal mercury, it is less active than the main portion of the amalgam.

The existence of these various phases may explain why no constant values for the ratio of the colloidal mercury to the tetramethyl ammonium group have been found, as each run has obviously been a mixture of a number of phases in varying proportions.

It will now be of interest to compare our results with those of Lewis and Kraus,[1] just published, on the potentials of sodium and sodium amalgam, although we made no serious attempt at accurate definition of the potentials measured, while they attained a remarkably high degree of accuracy. For the cell: Sodium amalgam (0.206 per cent.), normal Na ion, normal calomel electrode, Lewis and Kraus found an electromotive force of 2.1525 volts at 25° and for metallic sodium, normal Na ion, normal electrode, 2.9981 volts. In experiment 233, Table IV, we found for the cell: tetramethyl ammonium amalgam, 0.5 normal ion, 0.1 normal KCl, decinormal electrode, a maximum electromotive force of 2.57 volts at 0°. This would be equivalent to about 2.73 volts for conditions as in the experiments of Lewis and Kraus, excepting the concentration of the amalgam. The latter was not known in our experi-

[1] THIS JOURNAL, 32, 1459 (1910).

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ment, but was probably in the neighborhood of 1 per cent. It is, therefore, clear that the potential of our amalgam is decidedly greater than that of sodium amalgam of the same concentration, which conclusion is in harmony with the very much greater activity of our amalgam toward water and alcohol.

Reuter[1] found that the potential of potassium is 0.4 volt higher than that of sodium at —80°, which would indicate a difference of 0.6 volt at 25°. As a rough estimate, then, the potential of our amalgam should be about the same as that of potassium. From the observed behavior toward water, however, we should expect the potential to exceed that of potassium, but to fall somewhat short of that of rubidium. It is of passing interest, though of doubtful significance, that the molecular weight of tetramethyl ammonium, 74.1, falls between the atomic weight of potassium, 39.1, and rubidium, 85.45.

F. Monomethyl Ammonium Amalgam.

The polarization measurements of Le Blanc[2] indicated that an amalgam was formed by the electrolysis of an aqueous solution of monomethyl ammonium chloride. We had no difficulty in obtaining the amalgam. The electrolysis took place at ordinary temperature, with 0.25 ampere. The readily formed amalgam resembled ammonium amalgam in its properties. When a solution of *dry* monomethyl ammonium chloride in absolute alcohol was electrolyzed (experiment 55) at ordinary temperature, at 0° and at —9° amalgamation again occurred. At —9° the amalgam formed was pasty. The potential of the cell: *monomethyl ammonium* amalgam, 0.5 *N* monomethyl ammonium chloride, 0.1 *N* KCl, 0.1 *N* calomel electrode was measured, exactly as in the method above for the tetramethyl ammonium amalgam. The solvent in 229 was water and in 231 was absolute alcohol. "Series A" in each case contains measurements made while the polarizing current was on; "Series B" after the polarizing current had been cut off.

On examining these results, it is seen that here the potentials in contact with alcohol are less than those where water is the solvent; it was found that a similar result was obtained with ammonium amalgam; indeed the remarkable fact was discovered that ammonium amalgam is much more reactive toward absolute alcohol than toward water.

As tetramethyl ammonium amalgam was obtained very soon after this work was undertaken, almost immediately an extensive search for amalgams of other radicals was begun, with the hope that some might be found which would be more stable. Of eighteen additional radicals studied, only one, monomethyl ammonium, gave an amalgam which could be isolated. The others gave, in general, negative results. The salts so studied were:

[1] *Z. Elektrochem.*, 8, 801 (1902).
[2] *Loc. cit.*

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dimethyl ammonium chloride, trimethyl ammonium chloride, monoethyl ammonium chloride, tetraethyl ammonium chloride, propyl ammonium chloride, butyl ammonium chloride, iodomethyltrimethyl ammonium iodide, aniline hydrochloride, dimethylaniline hydrochloride, phenylenediamine hydrochloride, phenyldiazonium chloride, pyridine hydrochloride, tetraethylphosphonium iodide, tetramethylstibonium iodide, trimethylsulfinium iodide, hydroxylamine hydrochloride and hydrazine hydrochloride.

TABLE V.—ELECTROMOTIVE FORCES IN VOLTS.

Time, min.	229A.	229B.	Time, min.	231A.	231B.
0	0.023	2.369	0	0.161	1.952
1	...	1.646	..	...	...
2	...	1.655	2	...	1.372
4	...	1.666	4	...	1.314
6	...	1.666	6	...	1.340
7	...	1.670	..	...	...
..	...	...	8	...	1.318
9	...	1.623	..	...	...
..	...	...	10	...	1.323
11	...	1.569	12	2.126	1.311
13	2.099	1.556	..	...	...
15	2.099	1.504	14	2.082	1.260
17	2.153	1.512	16	1.889	0.387
19	2.153	1.481	18	1.915	0.300
21	2.335	1.481	20	1.915	0.269
23	2.282	1.471	22	1.933	...
25	...	1.471	24	1.924	...
27	2.479	1.460	27	1.952	...
28	2.369	...	..	...	...
30	...	1.455	..	...	...
33	...	1.085	..	...	...
34	...	0.842	..	...	...

G. Summary of Results.

1. Tetramethyl ammonium amalgam has been prepared by the electrolysis in the cold of solutions of tetramethyl ammonium chloride in absolute alcohol, using a mercury cathode.

2. The amalgam exhibits certain physical properties of metals to a high degree. It has a crystallin structure more or less pronounced under certain conditions. It is lighter than mercury, but does not expand or become inflated at or below 10°, as does ammonium amalgam.

3. While fairly stable at low temperatures, near 20° it decomposes rapidly, yielding trimethylamine as one of the decomposition products.

4. In contact with cold air, it becomes coated over with a white alkaline crust, due to oxidation.

5. Water reacts violently on the amalgam, producing hydrogen, colloidal mercury, and tetramethyl ammonium hydroxide.

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A study of this reaction affords evidence that more than one active phase exists in the amalgam.

6. The amalgam acts on aqueous solutions of ammonium, sodium, potassium and copper salts, and alcoholic solutions of copper and zinc salts, the tetramethyl ammonium group replacing these metals in the salts and setting free the metals themselves or forming the amalgams of these metals. With rubidium and cesium salts the action is more violent than with potassium salts of equivalent concentration, but there is replacement even in the case of the cesium salts. The tetramethyl ammonium radical possesses a solution tension comparable with that of potassium, but probably less than that of rubidium, and considerably less than that of cesium.

7. The rate of formation of the tetramethyl ammonium ion from the amalgam, in contact with absolute alcohol, is about 5 per cent. per minute at 0°.

8. The electrode potentials of the amalgam in contact with water solutions and in contact with alcoholic solutions of tetramethyl ammonium salts have been measured against a decinormal calomel electrode at 0°.

2.6 volts and 2.0 volts were the values of the electromotive force of the amalgam calomel electrode cell found in contact with alcoholic solutions; 2.4 and 1.7 volts were found in contact with aqueous solutions of tetramethyl ammonium salts as the values of these potentials. The two values in each case probably correspond to two phases, thus substantiating other evidence that more than one phase of the amalgam is present in the amalgam. The curves for these potentials have been plotted.

9. Besides the extensive work upon tetramethyl ammonium amalgam, search has been made for other possible amalgams. Of the substances investigated, the monomethyl radical yields an amalgam, and the potential of this amalgam against a decinormal calomel electrode has been measured. This amalgam, like ammonium amalgam, is less stable in contact with alcohol than with water. The dimethyl ammonium radical, according to potential measurements, may possibly form an amalgam under certain conditions. Tetraethyl ammonium probably forms a very unstable amalgam. Of all the other substances investigated, a number gave faint indications of amalgam formation, but none gave as positive results as the three substances mentioned above.

10. As set forth in the introduction, we have proposed the hypothesis that complex radicals, constituting the positive ions of salts, if electrically neutralized by the introduction of electrons, equal in number to the valence of the ion, will be substances having metallic properties. We have, however, given some reasons why it may be impossible to isolate such radicals. While our experiments have not yet led to the complete

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isolation of complex radicals, we have gotten a new amalgam of one such radical which is far more stable than either ammonium amalgam or monomethyl ammonium amalgam. Though this substance is a compound of carbon, hydrogen and nitrogen on the one hand and mercury on the other, it has true metallic properties. Inasmuch as ordinary binary alloys with true metallic properties are formed only from components which are *both* true metals we are warranted, we think, in concluding that the organic radicals in our amalgams are in the metallic state and, therefore, that *it is possible to prepare composit metallic substances from non-metallic constituent elements.*

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 63.]

THE EQUILIBRIUM BETWEEN NITRIC ACID, NITROUS ACID AND NITRIC OXIDE.

BY GILBERT N. LEWIS AND ARTHUR EDGAR.

Received December 22, 1910.

The decomposition of nitrous acid in aqueous solution according to the reaction

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

was first shown by Veley[1] to be reversible. A more exact study of the equilibrium was made by Saposhnikov[2] to whom we owe much of our exact knowledge of the nitrogen acids.

Saposhnikov studied not only the decomposition of nitrous acid according to the above reaction, but also the reverse reaction starting with nitric acid and nitric oxide, and obtained an equilibrium condition apparently independent of the direction of approach. However, the equilibrium constants which he obtained in numerous experiments with acids ranging from 0.05 *N* to 3.0 *N* were not entirely concordant, and in the stronger solutions, varied systematically with the concentration.

An exact knowledge of this equilibrium constant in dilute solutions is of great importance in the calculation of the free energy of nitrogen compounds. It has therefore seemed advisable, relying on Saposhnikov's proof that true equilibrium is established in this reaction independently of the direction of approach, to attempt a more accurate determination of this constant for at least one of the more dilute solutions. We have therefore investigated the final conditions established when a stream of nitric oxide is passed through a tenth-normal solution of nitric acid.

The method employed is a modification of one used by Saposhnikov. A slow stream of nitric oxide is passed through the nitric acid solution in a vessel which permits the measurement of the electrical conductivity

[1] *Chem. News*, 66, 175 (1892).

[2] *J. Russ. Phys. Chem. Soc.*, 32, 375 (1900); 33, 506 (1901).

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of this solution. From time to time the conductivity is measured until it reaches a constant value. Since the conductivity of the nitrous acid which is produced is almost negligible in the presence of nitric acid, the change in conductivity is very nearly proportional to the amount of nitric acid decomposed in the reaction

$$HNO_3 + 2NO + H_2O = 3HNO_2.$$

The form of the conductivity cell in which the reaction took place is represented in Fig. 1. Nitric oxide entered through the tube A, bubbled through the nitric acid which nearly filled the cell, and passed out through the bulb B. The liquid was thus constantly stirred and kept saturated with nitric oxide. The platinized platinum electrodes were convex from below in order to prevent their trapping bubbles of gas. Leads entered through glass tubes C and D which were filled with mercury. The upper electrode was situated several centimeters below the level of the liquid in order to avoid any change of conductivity due to changes in level of acid. The resistance capacity[1] of this conductivity cell was accurately determined by means of a tenth-normal sodium chloride solution and was constant throughout the experiments.

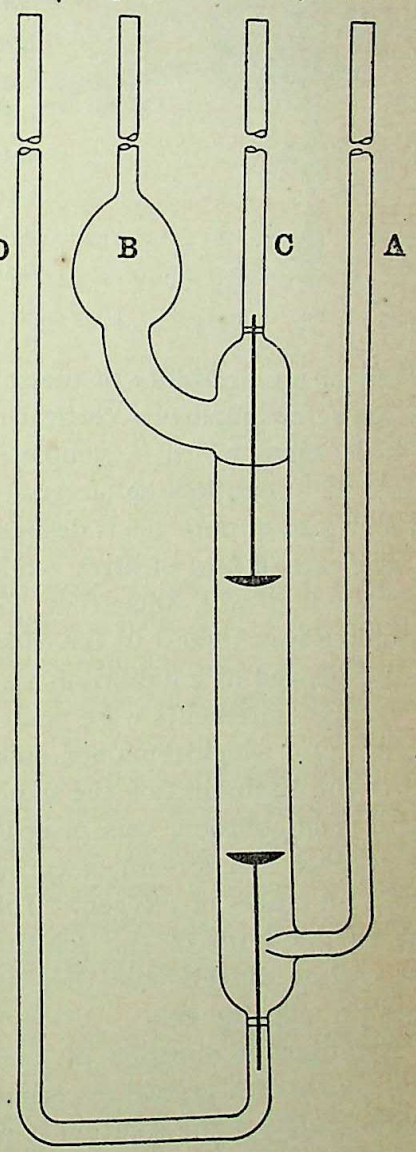


Fig. 1.

The solution of nitric acid was made from the best procurable nitric acid of commerce and contained no detectable impurities. Its concentration was 0.09957 normal.

Nitric oxide was prepared[2] by treating dry sodium nitrite with fifty times its weight of concentrated sulfuric acid in the presence of metallic mercury. The gas was washed with water and caustic soda and was stored over water in a gas reservoir of four liters capacity. This reservoir was kept in the same thermostat in which the measurements were

[1] The standardizing solution contained 5.8476 grams of NaCl per liter at 25°, and was assumed to have a specific conductivity of 0.01076.

[2] Cf. Emich, *Monatsh.*, 13, 73 (1892).

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made, and the gas thus entered the conductivity cell at the proper temperature, and saturated with water vapor.

The stream of nitric oxide was regulated by a needle valve of special design[1] shown in Fig. 2. A drum is made of a section of brass tubing to each end of which a brass disk is soldered, the upper one being sufficiently thin to permit considerable vertical play. Gas enters this drum through the tube A, which is soldered into the lower disk, and escapes through the tube B. The flow of gas through A may be regulated or entirely cut off by vertical motion of a cone which fits into A and is attached to the upper disk. On the outer side of this disk is soldered a socket which contains a tightly fitting ball. This ball is in turn rigidly attached to a screw which is threaded into a rigid arch attached firmly to the drum. On account of the flexibility of the thin upper disk of the drum, a movement of the screw imparts a vertical motion to the cone of the valve.

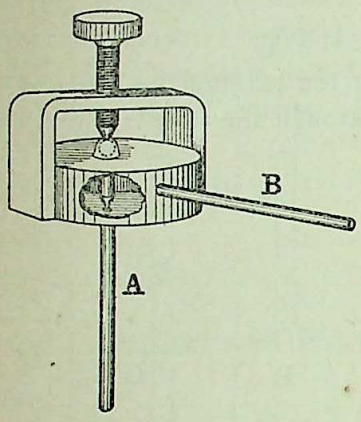


Fig. 2.

This valve, which is completely air-tight, and in which no packing is used, will doubtless be of service in other cases where a delicate control of a stream of pure gas is desired.

The rate of flow of nitric oxide, which by means of this valve could be regulated at will, was from 30–150 bubbles per minute. The rate of bubbling was highest in the early stages of the experiment and was gradually reduced as equilibrium was approached.

The measurements were made at 25.0° in a large thermostat, the temperature of which remained constant within 0.02°.

At the beginning of the experiment the cell, having been filled with nitric acid solution, was placed in the thermostat and the conductivity determined. A stream of carbon dioxide was then sent through to remove all traces of oxygen. This did not in any case appreciably affect the conductivity of the solution. By means of a three-way stopcock the carbon dioxide was then shut off and nitric oxide was allowed to flow through the cell.

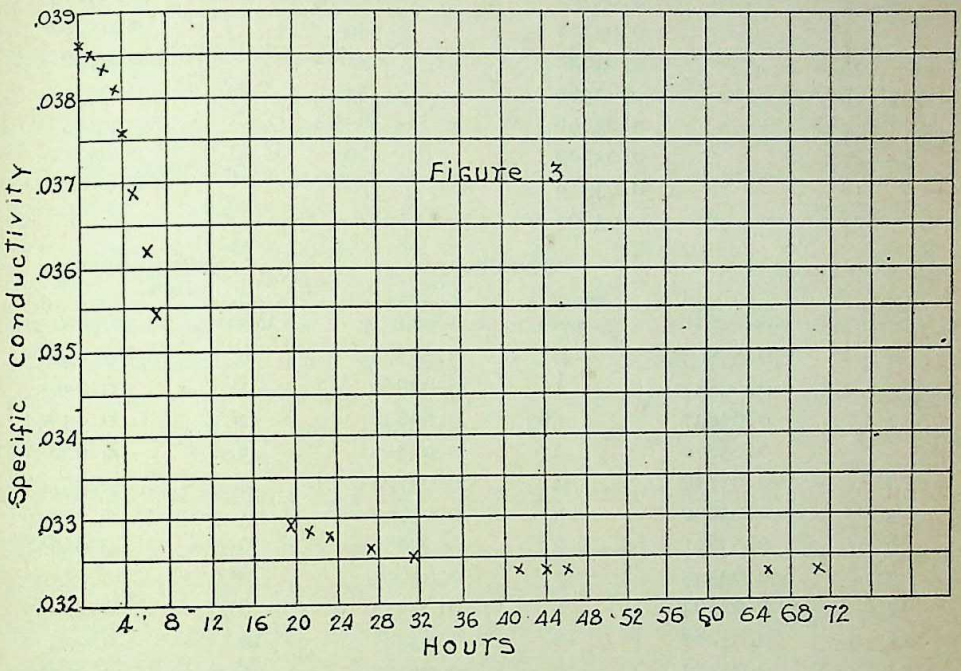
The time of duration of the experiments ranged from 50–70 hours. The course of a typical experiment is shown in Fig. 3, where the specific conductivity of the solution is plotted vertically and the duration of the experiment in hours horizontally. It is evident that equilibrium was

[1] The fundamental idea of a valve of this kind was first developed during an investigation carried on by one of the present authors in collaboration with Dr. C. A. Kraus.

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almost completely established at the end of 50 hours, the conductivity during the remaining 20 hours changing less than 0.1 per cent. It is remarkable that the reaction does not reach its maximum rate till after the lapse of several hours. It is hardly likely that this can be due to



slowness of saturation of the liquid with NO. It seems more probable that the reaction is in some unknown way autocatalytic. It should be mentioned also that the velocity of the reaction is increased by increasing the rate of bubbling of the gas. These phenomena were not further investigated.

Eleven experiments were made, of which six were not altogether satisfactory, owing to an insufficient supply of nitric oxide in the reservoir, condensation of water in the tube leading to the cell (this tube being for a short distance outside of the thermostat) and to other accidental causes. The results of the five remaining experiments, which were in all respects satisfactory, are given in the following tables.

EXPERIMENT 1.

Time in hours.	Specific conductivity.	Time in hours.	Specific conductivity.
0	0.03867	12	0.03371
1	0.03860	22	0.03280
2	0.03854	24	0.03266
3	0.03843	30	0.03249
4	0.03797	33	0.03243
5	0.03732	34	0.03236
6	0.03635	36	0.03234
7	0.03545	47	0.03234
8	0.03510	49	0.03235
9 1/3	0.03439		

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EXPERIMENT 2.

Time in hours.	Specific conductivity.	Time in hours.	Specific conductivity.
0	0.03870	26	0.03280
1	0.03863	28	0.03279
2	0.03843	30	0.03279
3	0.03782	$40^5/_6$	0.03274
4	0.03712	44	0.03268
5	0.03626	$51^1/_2$	0.03268
6	0.03568	54	0.03261
$7^1/_6$	0.03496	$65^1/_2$	0.03255
17	0.03320	69	0.03252
18	0.03318	$70^5/_6$	0.03244
21	0.03295		

EXPERIMENT 3.

Time in hours.	Specific conductivity.
0	0.03865
1	0.03851
2	0.03837
3	0.03812
4	0.03756
5	0.03690
6	0.03621
7	0.03545
$19^1/_2$	0.03294
21	0.03287
23	0.03274
$27^1/_2$	0.03257
$31^1/_2$	0.03253
$41^3/_4$	0.03240
44	0.03239
46	0.03238
$65^3/_4$	0.03234
$70^3/_4$	0.03234

EXPERIMENT 4.

Time in hours.	Specific conductivity.
0	0.03868
1	0.03862
$1^3/_4$	0.03848
3	0.03817
4	0.03771
5	0.03750
6	0.03681
7	0.03604
8	0.03554
18	0.03387
19	0.03377
$21^1/_6$	0.03353
23	0.03349
25	0.03299
28	0.03272
32	0.03260
42	0.03251
44	0.03252
$46^1/_2$	0.03249
53	0.03248
$55^1/_2$	0.03247
66	0.03244
$72^2/_3$	0.03245

EXPERIMENT 5.

Time in hours.	Specific conductivity.
0	0.03865
1	0.03857
$2^1/_4$	0.03843
3	0.03831
4	0.03787
5	0.03748
6	0.03658
$6^3/_4$	0.03586
$8^1/_2$	0.03457
10	0.03397
$11^3/_4$	0.03381
$20^3/_4$	0.03303
$24^3/_4$	0.03278
$27^1/_4$	0.03263
$31^1/_4$	0.03260
37	0.03251
$44^3/_4$	0.03247
$47^3/_4$	0.03241
$50^1/_2$	0.03238

The change in the specific conductivity in these five experiments as well as the initial and final values are given in the following table.

Number of experiment.	Initial conductivity.	Final conductivity.	Decrease in conductivity.
1	0.03867	0.03235	0.00632
2	0.03870	0.03244	0.00626
3	0.03865	0.03234	0.00631
4	0.03868	0.03245	0.00623
5	0.03865	0.03238	0.00627
Average,	0.038670	0.032392	0.006278

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It will be seen that the average deviation from the mean is 0.04 per cent. for the initial values, 0.13 per cent. for the final values, and only 0.47 per cent. for the decrease in conductivity, in which experimental errors are greatly magnified. The extremely satisfactory agreement in these experiments renders it certain that a true equilibrium is here established.

The conductivity of the final solution is due almost solely to the nitric acid present, for nitrous acid is a weak acid and is very little dissociated in the presence of the stronger acid. In order to calculate that small part of the conductivity due to the nitrous acid, we may as a first approximation consider the change of conductivity in the experiments proportional to the amount of nitric acid consumed. Starting with tenth-molal nitric acid, the conductivity changed from 0.03867 to 0.03239. Assuming that the nitric acid has decreased in the same proportion, we find that about 0.016 mol per liter has been decomposed. Each mol of nitric acid gives three mol of nitrous acid which is therefore present in the final solution to the amount of 0.048 mol per liter. The dissociation constant of nitrous acid may be taken[1] as $0.00045 = \frac{(H^+)(NO^-_2)}{(HNO_2)}$.

Since the final solution was about 0.083 molal in nitric acid and this acid may be taken as 84 per cent. dissociated, the concentration of hydrogen ion is 0.070 mol per liter. Substituting in the above equation this concentration and the concentration of nitrous acid which we found to be 0.048, we obtain 0.00031 as the concentration of nitrite ion. The concentration of hydrogen ion due to the nitrous acid obviously has the same value. The molecular conductivity at infinit dilution of nitrous acid is 412. Since the molecular conductivity is one thousand times the specific conductivity divided by concentration (in mols per liter), that part of the specific conductivity of our final solution due to nitrous acid is $412 \times 0.001 \times 0.00031$, or 0.00013.

Repeating this calculation, making use of this approximate value, as well as the more exact assumptions which we are about to discuss, gives 0.00032 for the concentration of nitrite ion, or 0.000132 for the conductivity due to the nitrous acid, which is practically identical with the result of the first approximation.

Subtracting this conductivity of the nitrous acid from the average final conductivity of our experiments gives 0.03226 as the conductivity of the nitric acid. In order to ascertain the exact concentration of nitric acid corresponding to this conductivity, we measured directly the conductivity of pure nitric acid, 0.08468 *N*, which had been estimated to give about the same conductivity as the nitric acid in the final solution. The specific conductivity of this solution was found to be 0.03291. From

[1] Abegg, *Handbuch anorg. Chem.*, 3, III, 144.

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this conductivity and that of our tenth-normal nitric acid, by a slight extrapolation the strength of acid having the specific conductivity 0.03226 was found to be 0.08299 *N*.

In order to obtain the most reliable value for the degree of ionization of nitric acid we have assumed it to be equal to that of potassium nitrate at the same concentration. The work of Noyes and Kato[1] shows that this gives a truer value than the one obtained directly from the conductivity of the acid. The degree of dissociation thus obtained, on the basis of Kohlrausch's potassium nitrate measurements, is 84.1 per cent.

The reaction under investigation may be written in the form

$$H^+ + NO_3^- + 2NO + H_2O \rightleftarrows 3HNO_2.$$

Regarding the activity of the water as constant, and also that of the nitric oxide, which is always present at the same pressure, we may write for the equilibrium constant

$$K = \frac{(HNO_2)^3}{(H^+)(NO^-_3)}.$$

The concentration of the nitrous acid which we have shown to be three times the difference between the initial and final concentrations of the nitric acid is 0.04974. Of this 0.00032 is in the form of ions, leaving 0.04942 as the concentration of the un-ionized nitrous acid. The concentration of the nitrate ion, namely 0.06983, is found by multiplying that of the nitric acid by the degree of ionization, and the concentration of hydrogen ion is this same value plus a small amount coming from the nitrous acid, making 0.07015.

The equilibrium constant is thus found to be 0.0246. This is the value of the constant obtained under the actual conditions of the experiments in which the nitric oxide was kept at atmospheric pressure. The barometric readings varied only slightly in the five experiments, the average being 0.992 atm. The nitric oxide, however, was saturated with water vapor at 25° of which the partial pressure was 0.031 atm. This leaves 0.961 as the partial pressure of the nitric oxide. In order to obtain the value of the equilibrium constant with nitric oxide at one atmosphere, we must divide the value given above by $(0.961)^2$, since two mols of nitric oxide enter into the reaction.

We thus obtain as a final value of the equilibrium constant at 25°, and under standard conditions, K = 0.0267.

The value obtained by Saposhnikov starting with nitric acid of the same concentration was 0.0175. If, however, we recalculate his results using the same value for the degree of dissociation of nitric acid that we have used, his value becomes 0.0208.

A few experiments which we have made with 0.2 *N* nitric acid seem to

[1] *Pub. Carnegie Inst.*, 03, 313 (1907).

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indicate a change in the equilibrium constant with the concentration, in the direction found by Saposhnikov, but further experiments will be necessary to decide this question.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 64.]

THE POTENTIAL OF THE CHLORINE ELECTRODE.

BY GILBERT N. LEWIS AND FRANK F. RUPERT.

Received January 16, 1911.

The potential of the chlorine electrode has been studied by numerous observers, but the various determinations are by no means in agreement with one another. Müller,[1] who has made the most recent and the most thorough investigation of this subject, has pointed out the chief cause of the observed discrepancies. Chlorine, in the presence of water, hydrolyzes according to the reaction which was first carefully studied by Jakowkin,

$$Cl_2 + H_2O = H^+ + Cl^- + HClO.$$

This hydrolysis takes place to a less extent in a solution of any chloride, and especially of hydrochloric acid, than in pure water, but nevertheless it occurs to a sufficient extent to affect the potential of the chlorine electrode, owing to the increase in concentration of chlorine ion. The change in potential due to this hydrolysis was calculated by Müller to be about $1^1/_2$ millivolts in 0.1 normal and 146 millivolts in 0.001 normal hydrochloric acid. The results of Müller for the potential of chlorine at atmospheric pressure against solutions of hydrochloric acid at four different concentrations are given in the following table. The potential in each case is measured against that of a hydrogen electrode in the same solution.

Conc.	Observed e. m. f.	Corrected e. m. f.	Calculated e. m. f.
1	1.366	1.366	...
0.1	1.485	1.486	1.477
0.01	1.546	1.599	1.594
0.001	1.587	1.733	1.712

The first column gives the concentration of the acid in equivalents per liter, the second the observed electromotive force, the third the same after the correction has been made for the increase of chloride ion due to hydrolysis of the chlorine, and the fourth shows the values calculated for the three lower dilutions from that at normal concentration. It is evident that Müller's correction for hydrolysis has to a large extent eliminated the deviations between the calculated and observed values. There remains, however, an uncertainty as to the true value of the poten-

[1] *Z. physik. Chem.*, 40, 158 (1902).

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tial of the chlorine electrode amounting apparently to one centivolt or more.

Another possible source of error was mentioned by Müller. It is well known that iodine combines to a large extent with iodide ion to form tri-iodide ion, and it is not improbable that to a certain extent chlorine takes part in a similar reaction, namely,

$$Cl^- + Cl_2 = Cl_3^-.$$

This reaction would diminish the concentration of the chloride ion in solution and by about the same percentage amount in each concentration. It would not therefore affect the difference between the potentials of chlorine in two different concentrations of hydrochloric acid, but it might nevertheless cause a considerable error in the determination of the absolute potential of the chlorine electrode.

It is obvious that both these sources of uncertainty in the potential of chlorine would to a large extent be avoided if, instead of chlorine gas at atmospheric pressure, chlorine at a relatively small partial pressure were used at the electrode, for the change in chloride ion concentration, due to the reactions above considered, would in both cases be nearly proportional to the partial pressure of the chlorine.

We shall describe in this paper the results of an investigation of the potential of chlorine gas at low pressures. In order to reduce the partial pressure of the chlorine, it was decided to mix it with some inert gas, and it was originally planned to use nitrogen for this purpose. However, in the preliminary experiments, air was used and since it behaved in all respects as a perfectly inert gas, it was used in all the experiments.

The mixture of chlorine and air was stored in a glass carboy of about 45 liters capacity. A glass tube fitting tightly into the neck of the carboy was cemented in by a substance which goes by the trade name of "caementium," composed entirely of inorganic materials. The upper end of this tube was joined to a stopcock. The carboy after partial exhaustion was filled with the desired amount of chlorine, and dry air was then forced in until the pressure inside the carboy exceeded the external pressure by about one-third of an atmosphere. A considerable amount of calcium chloride was always kept in the carboy to act as a drying agent.

The chlorine was prepared in three different ways: first, by the action of concentrated hydrochloric acid on manganese dioxide; second, by forming the solid hydrate of chlorine from gas prepared by the first method, and then decomposing the hydrate; third, by the action of concentrated hydrochloric acid on an excess of potassium permanganate at room temperature.[1] We have no reason to believe that there was any difference

[1] This method has been investigated by Graebe, *Ber.*, 35, 43 (1902), and Lewis and Wedekind, *Z. angew. Chem.*, 22, 580 (1909), and shown to give a gas that is free from the oxides of chlorine.

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in the potential of these three varieties of chlorine. In the preliminary measurements differences amounting to several millivolts, which were at first ascribed to impurities in the chlorine, proved later to be due, at least in large part, to an error of an entirely different character. The final series of measurements was made entirely with chlorine prepared by the third method. In every case the chlorine was thoroughly washed and dried before it entered the carboy. All connections between the source of chlorine and the carboy, as well as those between the carboy and the cell in which the potential was measured, were of glass, with the single exception of the cemented joint which we have already mentioned. Early experiments showed that the use of rubber or organic cements led to variable and incorrect results.

After the gas had remained in the carboy sufficient time to insure constancy of composition it was allowed to pass in a slow stream (about 5 cc. per minute) through the apparatus shown in Fig. 1. A is a washing device filled with acid of the same concentration as that used in the electrode chamber. It served to saturate the gas with moisture and also to remove any hydrochloric acid which might have remained in the gas. Passing through this portion of the apparatus the gas entered the electrode chamber at B; thence rising through the hydrochloric acid solution it passed out through the tube C. By means of the three-way cock D it could be then led off through the trap E or could be sent through the tube F to the apparatus for analyzing the gas, which is not shown in the figure.

The electrode chamber and the tube IK contained a solution of hydrochloric acid. The tube K was immersed in a vessel communicating with the standard electrode. Two stopcocks were placed in this tube and at least one of these stopcocks remained closed, the film of liquid remaining between the stopcock and its socket affording sufficient electrical contact. Lest, however, a potential difference establish itself between the two sides of the stopcock, two cocks were placed in series so that either one could be opened during the measurements. The electrode G was half immersed in the hydrochloric acid solution. It consisted of about $1^1/_2$ sq. cm. of platinum-iridium foil (15 per cent. iridium) and was welded to a platinum-iridium wire sealed through the glass stopper H. The gas which passed through the cell was analyzed by passing it through a solution of potassium iodide to absorb the chlorine, and titrating the iodine set free against thiosulfate. The residual gas was collected and measured in a buret over water. Analyses of the same mixture were frequently made throughout a period of several days, but no appreciable change of composition was ever observed.

In the first experiments the chlorine potential was measured against the normal electrode, the end of this normal electrode and the tube K

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of the cell shown in Fig. 1 being both immersed in an intermediate reservoir containing tenth-normal potassium chloride, when the cell was filled with tenth-normal hydrochloric acid, and twentieth-normal potassium chloride when twentieth-normal hydrochloric acid was used. A number of measurements were made with both these concentrations of acid and with

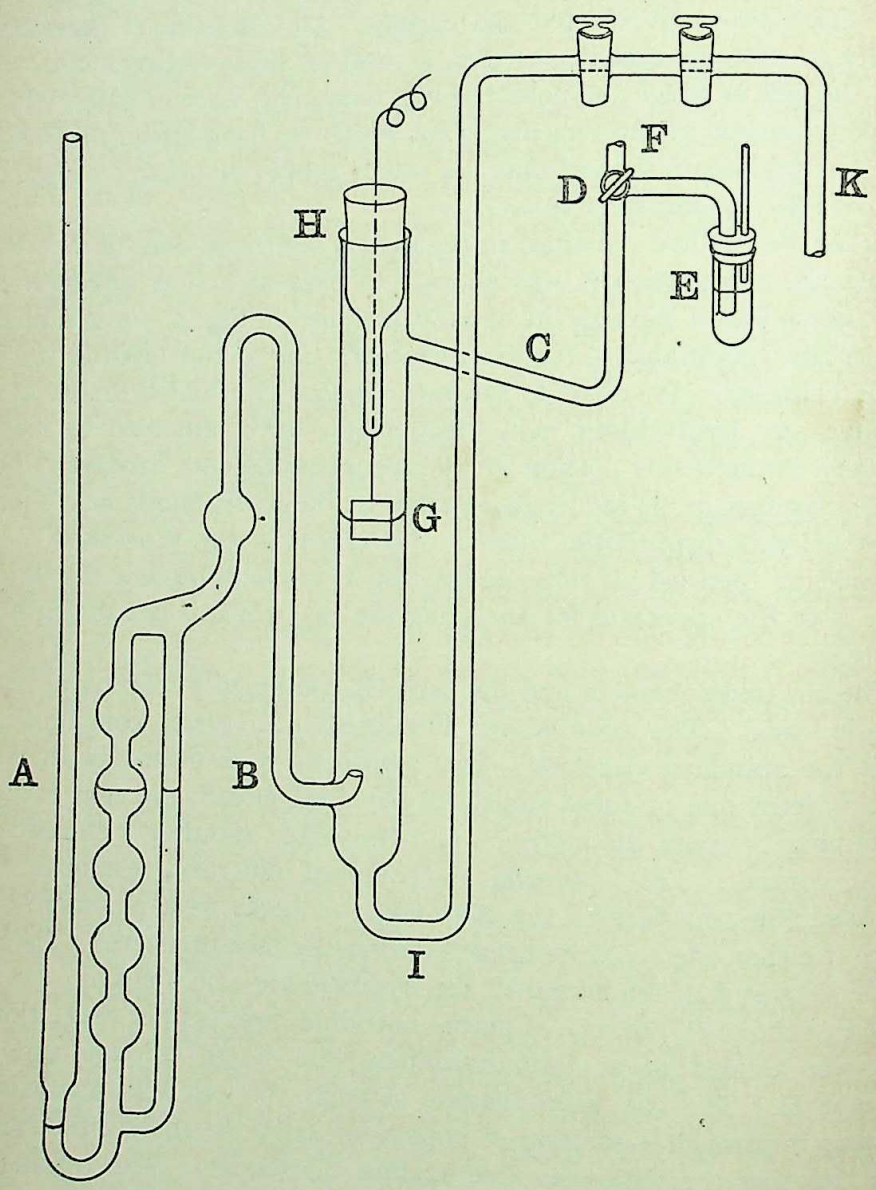


Fig. 1.

different pressures of chlorine gas ranging from 0.12–0.03 atmosphere. A single filling of the gas reservoir with chlorine served for a number of experiments, successive dilutions of the chlorine being made by partly exhausting the reservoir and refilling it with dry air under pressure.

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Altogether in these first experiments eleven measurements were made with tenth-normal, and ten with twentieth-normal hydrochloric acid. From the observed electromotive forces the potential of chlorine at atmospheric pressure against a normal solution of chloride ion was calculated. In this calculation the potential of the normal electrode was taken as zero and a correction was made for the potentials between the liquids. This calculation need not be discussed further here, because it will be treated in detail in connection with the final series of measurements. The value thus obtained for the potential of the chlorine electrode was 1.082 volts for the tenth-normal solution, with an average deviation of 0.001 volt, and 1.083 for the twentieth-normal solution with an average deviation of 0.003. These results were all obtained with chlorine prepared in part by the first and in part by the second of the methods described above. A later series of 13 measurements in tenth-normal hydrochloric acid, with chlorine prepared by the third method, at pressures ranging from 0.20–0.05 atmosphere, gave the value 1.082 with an average deviation of 0.002 volt. These results were sufficient to indicate a substantial agreement between the measurements in tenth- and twentieth-normal hydrochloric acid and to fix the absolute potential of the chlorine electrode within a few millivolts.

It seemed, however, desirable to investigate a little more closely the cause of the observed deviations between the individual measurements, especially as these differences did not appear to be due to any lack of constancy in the chlorine electrode itself. In the experiments of Müller the potentials only became constant to within one or two millivolts after the lapse of many hours, while in our experiments a much higher constancy was obtained in from one to two hours. In one experiment the platinum-iridium foil which served as electrode was removed from the cell and highly charged with chlorine by electrolysis. When replaced in the cell the electromotive force returned within an hour and a half to within a few tenths of a millivolt of its former value, thus indicating that the potential is very nearly if not quite independent of the previous treatment of the electrode.

The source of error was finally traced to changes in the liquid potentials. A standard electrode was made with mercury and calomel in a tenth-normal solution of hydrochloric acid and the potential of this electrode against the normal electrode was measured with tenth-normal potassium chloride as an intermediate electrolyte. The electromotive force of this combination was found to change on standing, due doubtless to the inter-diffusion of the electrolytes. On renewing the liquids in the connecting tubes of the electrode cells, and in the intermediate vessel, the original value was obtained. These experiments indicated that the deviations of the previous measurements of the chlorine potential among

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themselves might be largely or altogether due to changes in the liquid potentials, and that the best values from previous experiments were not, as we had supposed, those obtained after long standing, but the somewhat lower values reached after a comparatively short time.

In order to eliminate liquid potentials entirely we continued the series of measurements with chlorine prepared by the third method and with 0.1 *N* hydrochloric acid, the earlier results of which we have summarized above. Now, however, the measurements were made against the calomel electrode in 0.1 *N* hydrochloric acid instead of the normal electrode. The results of this change were extremely satisfactory. It was evident immediately that values much more constant and reproducible than those previously obtained could now be expected. The first experiment after this change was made with chlorine at a partial pressure of 0.049 atmosphere. The following table gives the several measurements of the electromotive force at the times (from the beginning of the experiment) given in the first column.

TABLE I.

Hours.	E. M. F.
1	1.0500
$2^{3}/_{4}$	1.0507
3	1.0508
$3^{1}/_{2}$	1.0508

New hydrochloric acid was now placed in the electrode vessel and the measurements were continued with the same chlorine mixture, with the following results:

TABLE II.

Hours.	E. M. F.
$^{3}/_{4}$	1.0507
$1^{1}/_{2}$	1.0509
2	1.0509
$6^{1}/_{2}$	1.0509
18	1.0506
$19^{1}/_{2}$	1.0507
$20^{1}/_{2}$	1.0507
22	1.0507
24	1.0508

Similar experiments were made with successive dilutions of the chlorine gas with equally satisfactory results. These results are given in Table III, in which the first column shows the percentage of chlorine by volume in the gaseous mixture; the second the atmospheric pressure, P, in millimeters; the third the partial pressure, p, of the chlorine in atmospheres; the fourth column gives the observed electromotive force E_1; the fifth the electromotive force E_2, calculated for chlorine at atmospheric pressure by the equation $E_2 = E_1 - \frac{RT}{2F} \ln p$.

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TABLE III.

% Cl_2.	P.	p.	E_1.	E_2.
4.88	763	0.0490	1.0508	1.0895
4.88	767	0.0492	1.0509	1.0896
4.88	770	0.0495	1.0510	1.0896
2.47	[760]	0.0247	1.0421	1.0896
2.47	767	0.0249	1.0424	1.0898
2.47	746	0.0243	1.0419	1.0896
1.258	748	0.0124	1.0330	1.0894
1.258	754	0.0125	1.0330	1.0893
0.619	772	0.00629	1.0242	1.0892
0.619	775	0.00631	1.0243	1.0893
0.293	772	0.00298	1.0154	1.0900
0.293	760	0.00293	1.0150	1.0899
0.293	760	0.00293	1.0150	1.0899
			Average,	1.0896

This series of results is eminently satisfactory. The average deviation of the figures in the last column from the mean is less than 0.0002 volt. Moreover, there is no apparent trend in the values as we proceed from the higher to the lower chlorine pressures. Indeed the small differences which exist between the values for different partial pressures of chlorine are doubtless due to inaccuracies in the analysis of the gas mixture. The agreement of the independent values obtained with the same gas mixture shows that our chlorine electrode is reproducible within about 0.0001 volt.

If our theory as to the cause of the early discrepancies in our work be true, we should expect the electromotive forces previously obtained to be concordant with those of Table III in those cases in which the boundaries between the electrolytes were known to have been freshly established. Four such cases were found in our note-book, belonging to the series of which the experiments in Table III form the conclusion. These four experiments are given in Table IV, where the columns have the same significance as in Table III, except that from the observed electromotive force is subtracted the measured potential between the normal electrode and the calomel electrode in tenth-normal hydrochloric acid, thus making these values comparable with those in Table III.

TABLE IV.

% Cl_2.	P.		E_1.	E_2.
19.75	758	0.197	1.0941	1.0907
9.85	[760]	0.0985	1.0837	1.0892
4.88	[760]	0.0488	1.0747	1.0892
4.88	[760]	0.0488	1.0752	1.0896
			Average,	1.0897

The agreement is sufficient. We may conclude therefore that the poten-

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tial of the chlorine electrode, within the limits of experimental error, changes with the partial pressure of the chlorine by the theoretical amount, when the chlorine pressure varies between 0.20 and 0.003 atm. Starting with the value given in Table III for the electromotive force of the cell,

$$\text{Hg, HgCl, HCl (0.1 } N\text{), } Cl_2 \text{ (1 atmos.); } E = 1.0896^1 \qquad \text{(A)}$$

we may proceed in two entirely different ways to calculate the normal electrode potential of chlorine. We determined as the electromotive force of the combination,

Hg, HgCl, KCl (N), KCl (0.1 N), HCl (0.1 N), HgCl, Hg; $E = 0.0243$ (B).

Combining this with the above cell, we have

Hg, HgCl, KCl (N), KCl (0.1 N), HCl (0.1 N), Cl_2 (1 atmos.); $E = 1.1139$ (C).

The potential between normal and tenth-normal potassium chloride will be neglected. That of HCl (0.1 N), KCl (0.1 N), is 0.0284.[2] We thus find for the above combination exclusive of liquid potentials; that is, for the combination,

$$\text{N. E.,}^3 \ Cl^- \text{ (0.086 } N\text{), } Cl_2 \text{ (1 atmos.); } E = 1.1423 \qquad \text{(D)}$$

if we take the degree of dissociation of tenth-normal HCl as 0.86, equal to that of KCl, for which assumption we have abundant evidence.

We may now make an entirely different calculation of the electromotive force of this same combination (D) from combination (A) which does not involve any liquid potentials. Since the concentration of chloride ion is the same in 0.1 N HCl as in 0.1 N KCl, the potential of the chlorine electrode against a 0.1 N KCl calomel electrode would be the same as that against the 0.1 N HCl calomel electrode except for liquid potentials, but the difference between the potential of the calomel electrode in N and 0.1 N KCl is 0.0528.[4] We have, then, only to add this value to the electromotive force of combination (A) to obtain once more that of combination (D), namely 1.1424. The agreement is excellent.

Finally we have only to reduce the results to normal concentration of chloride ion. From the Nernst equation we have

[1] The positive sign of E indictes the tendency of the current to pass from left to right.

[2] This value is obtained from the modified form of the Planck equation given by Lewis and Sargent, THIS JOURNAL, 31, 363 (1909). The equivalent conductivity of HCl (0.1 N) is taken as 389.9 (Lewis and Sargent), that of KCl (0.1 N) as 128.8 (Kohlrausch). The original equation of Planck leads to a very different value (0.0266) for this liquid potential.

[3] Normal electrode.

[4] This value is obtained from the measurements of Sauer, *Z. physik. Chem.*, 47, 146 (1904) at 18°, and the known temperature coefficients of the normal and decinormal electrodes.

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Cl_2 (1 atm.), Cl^- (0.086 *N*), Cl^- (*N*), Cl_2 (1 atm.); E = —0.0629

and adding this to combination (D) we find

N. E., Cl^- (*N*), Cl_2 (1 atm.); E = 1.0795

or

Cl_2 (1 atm.), Cl^- (*N*), N. E.; E = —1.0795.

Wilsmore[1] gives as the potential of the chlorine electrode against the normal electrode —1.134. Müller,[2] in his summary, gives a value which reduces to —1.0702 against the normal electrode. This value, however, was based on his measurements with normal hydrochloric acid. Between a hydrogen and a chlorine electrode both in 0.1 *N* hydrochloric acid, he obtained the electromotive force —1.4849. Assuming the hydrochloric acid to be 86 per cent. dissociated, this corresponds to a normal chlorine potential of —1.0761, and if we make Müller's correction for the hydrolysis of chlorine this value is raised to —1.0775, a value which differs by only 2 millivolts from our own.

Summary.

In order to eliminate complications due to hydrolysis of chlorine the potential of chlorine was measured at low partial pressures ranging from 0.2–0.003 atmosphere. Dry air used as a diluent behaved as a completely inert gas.

After the elimination of liquid potentials the potential of chlorine at low partial pressure was found to be constant and reproducible to about 0.0001 volt.

The values of the potential of chlorine at atmospheric pressure calculated from the potential at several low pressures agree among themselves with an average deviation from the mean of less than 0.0002 volt.

The electrode potential of chlorine at atmospheric pressure in chlorine ion at normal concentration was calculated from the observed electromotive forces by two independent methods. The results of these two methods were in excellent agreement, and the electrode potential of chlorine against the normal electrode is —1.0795, a value which is probably correct within two- or three-tenths of a millivolt.

This value differs widely from those given previously by Wilsmore and by Müller, but agrees within two millivolts with the value obtained by recalculation from the experiments of Müller in tenth-normal hydrochloric acid.

BOSTON, MASS.

[1] *Z. physik. Chem.*, 35, 291 (1900).
[2] *Loc. cit.*

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 65.]

TRANSFERENCE EXPERIMENTS WITH MIXTURES OF POTASSIUM CHLORIDE AND SULFATE IN AQUEOUS SOLUTION.

BY G. M. J. MACKAY.

Received December 27, 1910.

CONTENTS: 1. Plan of the Investigation. 2. Description of the Apparatus and of the Transference Experiments. 3. Preparation of the Solution. 4. Method of Analysis. 5. The Transference Data and Calculated Transference Numbers. 6. Accuracy of the Results. 7. Relative Conductance and Ionization of the Two Salts in the Mixture Calculated from the Transference Values. 8. Relative Conductance and Ionization of the Two Salts in the Mixture Calculated from Their Conductance in Water. 9. Summary.

1. *Plan of the Investigation.*—The object of this investigation was to study further, by means of transference experiments, the validity of the empirical principle which seems to determin the conductance and ionization of the separate salts in mixtures of them in aqueous solution. This principle, first stated and tested with reference to uniunivalent salts with a common ion by Arrhenius,[1] tested further by the conductivity investigations of MacGregor, McIntosh, Archibald, and McKay,[2] and shown by Noyes[3] on the basis of existing data to apply also to unibivalent salts, even though the mass-action law require a very different effect, may be stated as follows: In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture.

The previous tests of this principle have, however, only shown that the sum of the conductances of the two salts in the mixture is substantially equal to that calculated by the principle; and they do not exclude the possibility, at any rate in a mixture of a uniuni- and a unibivalent salt, that there may be a compensation resulting from the fact that one salt is more ionized, and the other less ionized, than the principle requires. Transference experiments, however, should enable the conductance of the ions in the mixture to be separately determined. Thus, in a mixture of potassium chloride and sulfate, the transference numbers T_{Cl} and T_{SO_4} for the chloride and sulfate (*i. e.*, the number of equivalents of Cl or SO_4 transferred per faraday of electricity) are evidently given by the expressions:

$$T_{Cl} = \frac{C_{Cl^-}\Lambda_{Cl^-}}{C_{Cl^-}\Lambda_{Cl^-} + C_{SO_4^=}\Lambda_{SO_4^=} + C_{K^+}\Lambda_{K^+}} \text{ and}$$

$$T_{SO_4} = \frac{C_{SO_4^=}\Lambda_{SO_4^=}}{C_{Cl^-}\Lambda_{Cl^-} + C_{SO_4^=}\Lambda_{SO_4^=} + C_{K^+}\Lambda_{K^+}}$$

[1] *Z. physik. Chem.*, 2, 285 (1888); 31, 218 (1899).

[2] *Trans. Nova Scotia Inst. Science*, 9 and 10 (1895–1899).

[3] *Z. physik. Chem.*, 52, 635 (1905).

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where C_{Cl^-}, $C_{SO_4^=}$, and C_{K^+} represent the equivalent concentrations, and Λ_{Cl^-}, $\Lambda_{SO_4^=}$ and Λ_{K^+} the equivalent conductances, in the mixture of the ions represented by the subscripts. We have therefore for the ratio of the transference numbers:

$$\frac{T_{Cl}}{T_{SO_4}} = \frac{C_{Cl^-}\Lambda_{Cl^-}}{C_{SO_4^=}\Lambda_{SO_4^=}} = \frac{C_1\gamma_1\Lambda_{Cl^-}}{C_2\gamma_2\Lambda_{SO_4^=}},$$

where C_1 and γ_1 represent the equivalent concentration and ionization of potassium chloride, and C_2 and γ_2 the corresponding values for potassium sulfate. Determinations of the relative quantities of chloride and sulfate transferred will therefore give the ratio of the specific conductances ($C\Lambda$) of the two ions. Moreover, if their equivalent conductances be assumed known (for example, equal to those known to be true at zero concentration) the results will show the ratio of the ionization of the two salts in the mixture.

With these purposes in view this investigation was carried out. It was undertaken at the suggestion of Prof. A. A. Noyes; and I desire to express my indebtedness to him and also to Prof. W. C. Bray, of this laboratory, for the assistance given me in connection with the experimental work and in the preparation of this article for publication.

2. *Description of the Apparatus and of the Transference Experiments.*— The apparatus employed in the final experiments was that previously used in this laboratory by Dr. E. W. Washburn and described by him in THIS JOURNAL, 31, 330 (1909). It is represented in Fig. 1.

The width of the tubes was about 2 cm. and the length between the anode and cathode was about 1 meter. One tube was fitted to the other at D by means of a ground glass joint. Each electrode compartment could be separated from the middle part of the apparatus by means of a large glass stopcock, whose bore was large enough not to make a constriction in the tube.

The anode A consisted of a coil made of about ten meters of fine silver wire. The cathode C consisted of a silver plate which had been chloridized on the surface by electrolysis, and was held in place by a stout silver wire welded to it and passing through a rubber stopper; on the top of the plate were placed several grams of freshly precipitated silver chloride which had been well washed, first with pure water, and finally with the solution under investigation. These electrodes served to prevent the separation of oxygen and hydrogen at the electrodes and to provide for the formation of silver chloride alone at the anode and its reduction to silver at the cathode. Hence the total result of the passage of a current of electricity was an increase at the cathode in the concentrations of K and Cl and a decrease in that of SO_4, and the opposit changes at the anode. The solution at the anode therefore grows lighter and that at the cathode heavier; hence to prevent stirring the

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anode was placed at the top of the open arm of the U-tube and the cathode at the bottom of the straight tube.

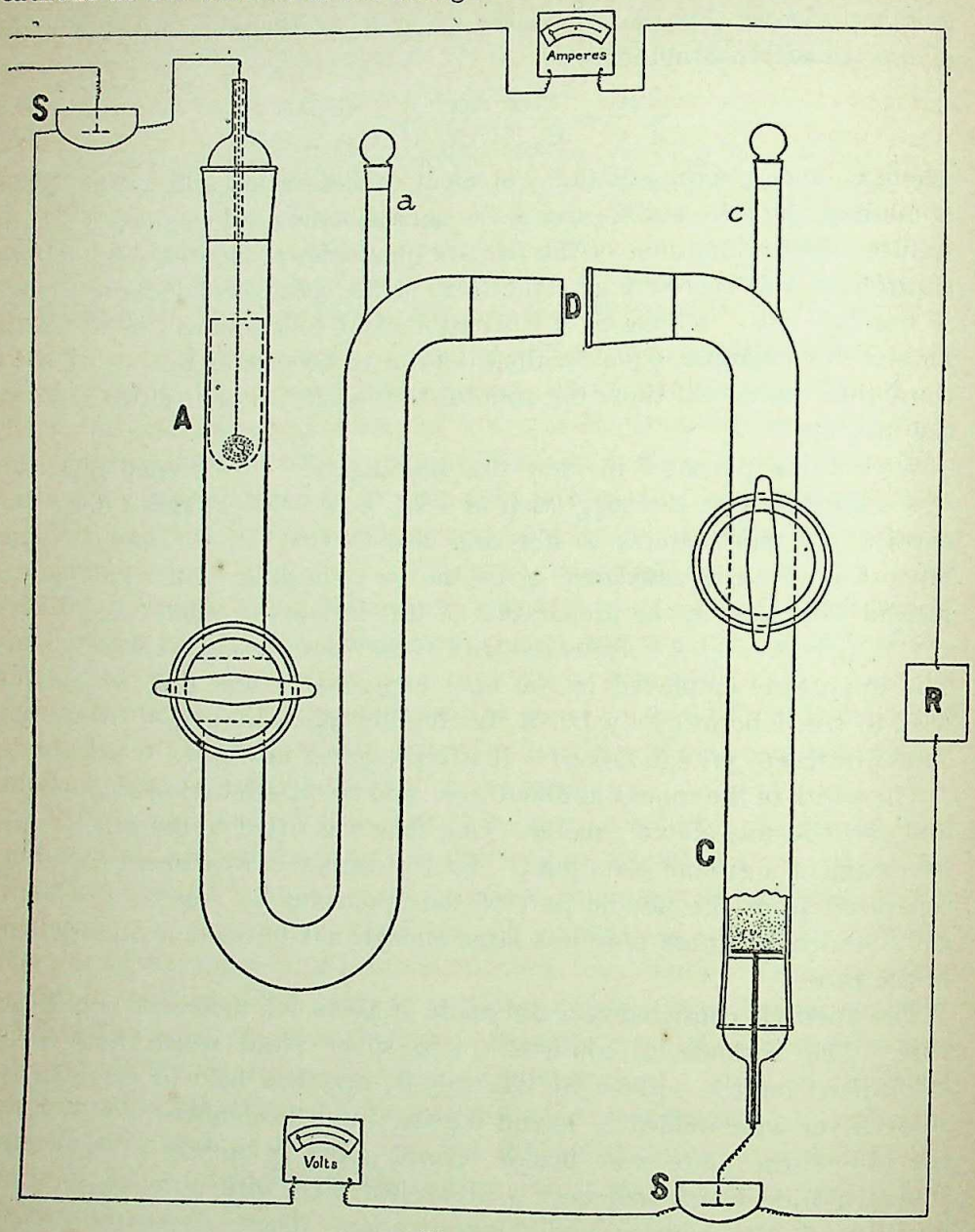


Fig. 1.

The coulometers S, S used consisted of platinum dishes partially filled with a 15 per cent. silver nitrate solution, just beneath the surface of which was placed a horizontal silver plate (to serve as anode) which was wrapped with filter paper, and supported by a silver rod riveted through it. One coulometer was placed on each side of the apparatus. In this way any leakage of current in the apparatus itself could be at once detected.

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As it was found that there was likely to be mixing of the electrode portion with the middle portion, especially on the cathode side, a piece of coarse-mesh silk cloth was placed in each stopcock, being held in place by a very thin ring of hard rubber. The ring was placed in that part of the stopcock nearer the electrode, so that, even if there were any selective transmission of the ions or any electrical endosmose (which in view of the coarse mesh was very improbable), the experiment would not be vitiated, inasmuch as the electrode portion was taken so as to extend from the electrode to the side of the stopcock farther from it.

The method of procedure was as follows: After filling the tubes with the solution, the ground joint and the glass stoppers were painted with paraffin, and the electrode ends were covered with wide rubber tubing, through which the leads passed. The whole apparatus, rigidly supported, was then immersed in a large thermostat at 18°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After about twenty minutes when all temperature differences had become equalized, the electrodes were connected in series with a lamp, an ammeter, and the two coulometers, between terminals of 110 volts potential difference. The ammeter was in circuit for convenience only, as the coulometers were depended upon wholly for measurement of the current. After the current had been passed for a suitable time, it was cut off and the stoppers were turned through 90°, thereby completely separating the electrode compartments from the middle portions. The three middle portions were then removed by a pipet through the small vertical arms.

The electrode portions were next removed from the apparatus. For this purpose the whole apparatus was taken out of the thermostat, the stopcocks were opened, and the two tubes separated, the openings being closed by rubber stoppers. The anode lead was cut and the coil of wire allowed to drop down into the solution, after which all the stoppers were well paraffined to prevent leakage, and each tube well shaken so as to insure thorough mixing. In some cases it was necessary to introduce a piece of glass tubing, in order to break the cloth diaphragm. The tubes were then cleaned thoroughly on the outside with alcohol and ether, and weighed (without the rubber stoppers). The solution was then poured and rinsed into a glass-stoppered flask, being filtered to retain the silver chloride and silver particles, which were subsequently weighed. The tubes were then cleaned inside with water, alcohol, and ether, and weighed again together with the electrode. From the difference in the weights the weight of the solution was obtained, allowance being made for the weight of the silver chloride collected on the filter, the silver anode and the glass rod. A known portion of the solution was then evaporated and analyzed as described below.

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The middle portions were not analyzed by the same time-consuming procedure, and it seemed unnecessary to do so. A method of titration was employed instead, comparative determinations being made with the original and electrolyzed solution. This consisted in adding a known weight of a standard solution of silver nitrate, using such a quantity that a very small excess of silver was left in the mixture. This mixture was then warmed and filtered through a Gooch filter into a flask, where the filtrate was titrated with a very dilute potassium thiocyanate solution, using ferric alum as an indicator. The final titration in the case of the middle portions was carried to the same shade of color as in the case of the original solution, thus enabling small differences in the chloride content to be detected. Each portion was titrated in duplicate.

When any difference was found to exist between the chloride content in the middle portions and in the original solution, mixing was assumed to have occurred, and the experiment was discontinued. When the chloride content was found to be the same, however, the analyses of the electrode portions were proceeded with, on the assumption that no mixing had occurred.

Three experiments, judging from the constancy of the middle portions and other external evidence, were successfully completed, though in one of these the cathode portion was not analyzed, owing to an accident. Unfortunately the work had to be broken off before more experiments could be made. It is believed, however, that the results obtained are sufficient to afford reliable conclusions.

3. Preparation of the Solution.—The potassium chloride and sulfate used were obtained from Eimer & Amend as being of the highest grade. The samples were crystallized twice from hot water, and were ignited in large platinum dishes. About ten liters of solution were made up at one time by weighing out the proper amount of the salts and adding the necessary weight of water.

4. Method of Analysis.—The method of analysis employed consisted in evaporating the portions of solution to dryness and heating the residue to about 500° to get the total weight of salt, and then determining the chloride in the residue by precipitating it with silver nitrate and weighing the silver chloride in Gooch crucibles. After much preliminary experimenting, which showed the impracticability of making the evaporation in a platinum dish (owing chiefly to the creeping of the salt), the following process was adopted.

Two round-bottomed 250 cc. flasks of Jena glass were well steamed out in order to get rid of the more soluble portions of the glass. They were then washed with soap and water and finally with distilled water, and were heated in an electric furnace over night to a temperature of about 500°. They were then removed, a little dry air being blown into them

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to displace any moist air that might have remained, and they were hung inside a bell jar containing calcium chloride by means of platinum wires which were attached to the necks of the flasks. After being in the desiccator for 4 hours they were weighed, one of the flasks serving as a counterpoise. The whole treatment (except the steaming) was then repeated until two consecutive weighings differed by not more than 0.2 mg.l but the flasks seldom had to be weighed more than twice. 70 or 80 grams of solution were then introduced into one of the flasks, which was placed in a bath of lard. The bath was kept slightly above 100° until the solution had evaporated, then the temperature was gradually raised to about 250° in order to dry the residue thoroughly and so prevent spattering, which otherwise occurred when the flasks were placed in the furnace. The flasks were then lifted out of the lard, allowed to drain, and washed first with benzine and then with soap and water as before. They were then heated in the electric furnace to 500°, and treated otherwise like the empty flasks, consecutive weighings being always made until they were practically identical. At first the counterpoise flask was subjected to the same treatment as the other, but afterwards, as this was found to be unnecessary, it was left in the desiccator during the evaporation.

This method was found by trial experiments to give very accurate results, the maximum error in the weights being about 0.4 mg., which corresponded to a percentage error of less than 0.02 per cent. of the weight of residue after evaporation.[1]

In order to determin the chloride present, the residue from the evaporation was dissolved, the solution was filtered and precipitated with silver nitrate, and the resulting precipitate collected in a platinum Gooch crucible, dried, and weighed. All the analytical precautions advised by Richards[2] in his work on the "Revision of the Atomic Weights of Sodium and Chlorine" were observed.

5. The Transference Data and Calculated Transference Numbers.—The following tables contain the experimental data. All weights were reduced to the vacuum standard. The atomic weights employed are O = 16.00, Ag = 107.88, Cl = 35.46, K = 39.10, S = 32.07.

Table I contains analytical data for the original solutions, of which

[1] The results of one of the trial experiments were as follows: 2.9658 grams of a mixture of potassium chloride and potassium sulfate were dissolved in about 100 cc. of water, and the solution was evaporated in a weighed flask as just described. The difference in the weights of the flask and the counterpoising flask before evaporation, as determined successively, was 10.6307, 10.6303, 10.6303, and after evaporation, 13.5956, 13.5953, 13.5963, the respective differences being 2.9649, 2.9650, 2.9660. The most probable weight is the last; this differs from the weight of salt started with by only 0.2 mg. or less than 0.01 per cent. If the first two weights were taken the error would be about 0.03 per cent.

[2] *Carnegie Institution Publications*, 69, 17 (1907); THIS JOURNAL, 27, 492.

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two were used in the three transference experiments that were successfully completed.

TABLE I.—DATA RELATING TO THE COMPOSITION OF THE ORIGINAL SOLUTIONS.

	Solution used in Expts. I and II.	Expt. III.
Weight of solution analyzed	100.20	101.80
Weight AgCl found	2.8222	2.8704
Corresponding weight KCl	1.4680	1.4931
Weight KCl + K_2SO_4 found	3.1836	3.2380
Weight K_2SO_4 (by difference)	1.7156	1.7449
Weight water (by difference)	97.016	98.562
Density 18°/18°	1.0232	1.0231
Equiv. KCl per liter at 18°	0.2008	0.2010
Equiv. K_2SO_4 per liter at 18°	0.2008	0.2010
Specific conductance at 18°	0.03647	0.03658

Table II contains the data of the transference experiments and the values of the transference numbers calculated from them. All the numbers in the table (except those in the last two rows) represent weights in grams corrected for air buoyancy. The temperature during the electrolysis was 18°. In experiment I the analysis of the cathode portion was not completed. The middle portions remained in all these experiments substantially unchanged.[1]

TABLE II.—DATA OF THE TRANSFERENCE EXPERIMENTS AND CALCULATED VALUES OF THE TRANSFERENCE NUMBERS.

	Expt. I.	Expt. II.		Expt. III.	
	Anode.	Anode.	Cathode.	Anode.	Cathode.
Ag in coulometer	0.6550	0.6523	0.6523	0.8773	0.8773
Whole portion	73.44	88.81	116.66	87.54	86.79
Portion analyzed	68.47	81.90	108.10	82.57	75.99
Residue (KCl + K_2SO_4)	1.9923	2.4080	3.6257	2.3745	2.6564
AgCl obtained	1.3600	1.7429	3.6078	1.5535	2.8615
KCl in whole portion, final	0.7588	0.9831	2.0253	0.8567	1.7000
KCl in whole portion, original	1.0789	1.3043	1.7061	1.2880	1.2688
KCl in whole portion, difference	−0.3201	−0.3212	+0.3192	−0.4313	+0.4312
KCl equiv. to Ag. in coulometer	0.4527	0.4508	0.4508	0.6064	0.6064
K_2SO_4 in whole portion, final	1.3782	1.6281	1.8875	1.6607	1.3339
K_2SO_4 in whole portion, original	1.2609	1.5243	1.9939	1.5052	1.4828
K_2SO_4 in whole portion, difference	+0.1173	+0.1038	−0.1064	+0.1555	−0.1489
Transference number for Cl	0.2929	0.2875	0.2919	0.2887	0.2888
Transference number for SO_4	0.2217	0.1970	0.2019	0.2194	0.2101

[1] This is shown by the following values, which represent the percentage difference between the quantities of silver nitrate solution consumed in the titration of the middle portion and of an equal weight of the original solution. M_C denotes the middle portion adjoining the cathode portion, and M_A the middle portion adjoining the anode portion.

	Expt. I.	Expt. II.	Expt. III.
M_C	....	+0.01 per cent.	+0.05 per cent.
M_A	−0.06 per cent.	+0.10 per cent.	−0.04 per cent.

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6. Accuracy of the Results.—An inspection of the last two rows of Table II shows that the five values obtained for the transference number of the chloride ion agree fairly satisfactorily. The mean of these five values is 0.2900, the average deviation of the separate value from this mean being 0.0020; or omitting the first value, which is probably less reliable, the mean is 0.2892, and the average deviation of the separate values from this is 0.0014. As an expression of the best value and its probable accuracy, 0.289 ± 0.001 will therefore be adopted. The values for the sulfate ion, which it may be recalled were obtained not directly, but by difference, are so discordant as to be of little significance[1]—a fact for which there is no obvious explanation. Therefore only the values for the chloride ion will be considered in the following discussion.

7. Relative Conductance and Ionization of the Two Salts in the Mixture Calculated from the Transference Values.—If we make the assumption that the *relative* mobilities of the potassium and chloride ions are the same in the mixture of the two salts as in a dilute solution of potassium chloride, we may calculate the fraction of the electricity transported by the ionized portion of the potassium chloride simply by dividing the transference number (0.289 ± 0.001) for the chloride ion in the mixture by that (0.504)[2] for the chloride ion in potassium chloride. We thus obtain $T_{KCl} = 0.573$ for the fraction of the electricity carried by the ions of the potassium chloride; and by subtracting this from unity, we obtain $T_{K_2SO_4} = 0.427$ for the fraction of the electricity carried by the ions of the potassium sulfate.[3] By multiplying these transference numbers by the specific conductance (L) of the mixture (0.03652, see Table I), the (partial) specific conductance of the two separate salts in the mixture are found to be $L_{KCl} = 0.02093$ and $L_{K_2SO_4} = 0.01559$. The ratio of these two partial conductances or of the two transference numbers is 1.342.[4] If we divide this ratio by the ratio of the values of the

[1] Compare the foot-note on the following page.

[2] Bein, *Z. physik. Chem.*, 27, 50 (1898). Jahn and Bogdan, *Ibid.*, 37, 684 (1901). Cf. Noyes and Sammet, THIS JOURNAL, 24, 965 (1902).

[3] The fraction of the electricity carried by the sulfate ion may be calculated from this quantity by multiplying it by the transference number for pure potassium sulfate. This fraction becomes 0.220, if the transference number be taken as 0.514 in correspondence with the conductances of the ions at zero concentration. It becomes 0.217, if the transference number 0.507 found for a 0.2 normal solution be employed (Noyes, THIS JOURNAL, 23, 52 (1901)). These values will be seen to agree with two of the five experimental values recorded in the last row of Table II.

[4] The error in this ratio corresponding to the error ±0.001 in the transference value 0.289 is ±0.011. A larger and more uncertain error, however, probably arises from that in the assumed transference number 0.504. If it be assumed that, owing to hydration of the ions in the mixture or to any other cause, this value is in error by ±0.005, the ratio 1.342 would be in error from this cause by ∓0.027.

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equivalent conductances of the two salts at zero concentration,[1] we shall evidently obtain the ratio of the ionization of two salts in the mixture. That is:

$$\frac{\gamma_{KCl}}{\gamma_{K_2SO_4}} = \frac{L_{KCl}/\Lambda_{o\,KCl}}{L_{K_2SO_4}/\Lambda_{o\,K_2SO_4}} = \frac{0.573/130.1}{0.427/133.0} = 1.372$$

8. Relative Conductance and Ionization of the Two Salts in the Mixture Calculated from their Conductance in Water.—It remains now to calculate, by means of the principle stated in the first paragraph of this article, from the ionization values for the separate salts the ionization of each of them in the mixture, and to compare the result with that derived from the transference data.

The ionization γ of the separate salts was first calculated by the equation $\gamma' = \Lambda/\Lambda_o$ (the conductance ratio), and also by the unquestionably more exact equation $\gamma'' = \Lambda\eta/\Lambda_o\eta_o$ (where η represents the viscosity of the solution and η_o that of pure water). For this purpose the data given in the second to fifth columns of the following table were used; and the results given in the last four columns were obtained.

TABLE III.—CONDUCTANCE, VISCOSITY AND IONIZATION VALUES FOR POTASSIUM CHLORIDE AND SULFATE AT 18°.

Equiv. conc (C).	Λ at 18°.		η/η_o at 18°.		$\gamma' = \Lambda/\Lambda_o$.		$\gamma'' = \Lambda\eta/\Lambda_o\eta_o$.	
	KCl.[2]	K_2SO_4[3]	KCl.[4]	K_2SO_4.[4]	KCl.	K_2SO_4.	KCl.	K_2SO_4.
1.00	98.27	71.6	0.9820	1.1012	0.755	0.538	0.742	0.593
0.50	102.41	78.5	0.9898	(1.052)	0.787	0.590	0.779	0.621
0.40	(103.8)	(80.7)	(0.992)	(1.042)	(0.798)	(0.607)	(0.792)	(0.632)
0.20	107.96	87.8	0.9959	(1.021)	0.830	0.660	0.826	0.674
0.10	112.03	94.9	0.9982	1.0111	0.861	0.714	0.859	0.721
0.00	130.10	133.0	1.0000	1.0000	1.000	1.000	1.000	1.000

The two sets of values of $1/\gamma$ for each salt were then plotted against those of $(C\gamma)^{1/2}$, which is advantageous since a nearly linear graph is thereby obtained. From these plots values of γ corresponding to any given value of $C\gamma$, could be readily derived.

A preliminary estimate was next made of the concentration C_K of the (common) potassium ion in the mixture of potassium chloride and sulfate

[1] These have been calculated from $\Lambda_K = 64.6$ and $\Lambda_{Cl} = 65.5$ as given by Kohlrausch (*Z. Electrochem.*, 13, 333 (1907)), and $\Lambda_{SO_4} = 68.4$, a value derived in this laboratory through a consideration of all available data for the sulfates of univalent metals. It is to be noted that this calculation involves the assumption that the *ratio* of the conductances of the ions of the two salts is the same in the mixture in question as it is at zero concentration.

[2] Data of Kohlrausch and Maltby, *Landolt-Börnstein-Meyerhoffen Tabellen*, p. 744. Those at 0.40 normal were obtained by graphical interpolation.

[3] Data of Kohlrausch and Grüneisen, *Ibid.*, p. 745.

[4] Data of Grüneisen, *Wissensch. Abh. phys. techn. Reichsanstalt*, 4, 239–66 (1905). Those for K_2SO_4 at 0.5, 0.2, and 0.05 normal and for both salts at 0.04 normal were interpolated.

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in question; thus the values of the ionizations of the two salts was provisionally assumed to be 80 and 60 per cent. respectively, which gives approximately $C_K = 0.28$, since the concentration C of each salt was 0.2009. From the plots more nearly correct ionization values (γ_1 and γ_2) for the two salts corresponding to this ion concentration were then obtained; and from these values a new value of C_K was calculated (by the equation $C_K = C(\gamma_1 + \gamma_2)$). From this new value of C_K corresponding values of γ_1 and γ_2 were again derived, the process being repeated till the assumed value of C_K corresponded completely with those of γ_1 and γ_2 derived from it.

The partial specific conductances of the salts were calculated[1] from these ionization values by multiplying each of them by the concentration (0.2009) and by the appropriate Λ_0 value (130.1 for KCl and 133.0 for K_2SO_4). The products so obtained were, in the case of these values derived by assuming that $\gamma = \Lambda\eta/\Lambda_0\eta_0$, divided by the viscosity of the mixture (1.017);[2] but this was not done in the case of those derived by assuming $\gamma = \Lambda/\Lambda_0$.

The values of the conductance and ionization so obtained and the ratios of them are given in Table IV, together with those derived from the transference numbers as described in the preceding section.

TABLE IV.—VALUES OF THE SPECIFIC CONDUCTANCE AND IONIZATION OF POTASSIUM CHLORIDE AND SULFATE IN THE MIXTURE.

	Calculated by the principle of ionization in mixtures		Derived from the transference and conductance data.
	assuming $\gamma = \Lambda/\Lambda_0$.	assuming $\gamma = \Lambda\eta/\Lambda_0\eta_0$.	
L_{KCl}	0.02102	0.02052	0.02093
$L_{K_2SO_4}$	0.01587	0.01644	0.01559
Sum	0.03689	0.03696	0.03652
Ratio	1.325	1.248	1.342
γ_{KCl}	0.804	0.797	...
$\gamma_{K_2SO_4}$	0.595	0.625	...
Ratio	1.351	1.275	1.372

A comparison of the last two columns in this table shows that the actual partial conductance (as derived from the transference and conductance data) of the potassium chloride is 2.0 per cent. larger, and that of the potassium sulfate is 5.2 per cent. smaller, than that calculated under the assumption that $\gamma = \Lambda\eta/\Lambda_0\eta_0$ from the principle of ionization in mixtures. Assuming the correctness of the transference data and

[1] It should be mentioned that, though ionization values have been employed in these calculations, the results are only slightly influenced by a considerable variation in the Λ_0 values employed. The principle of ionization in mixtures in question is substantially a principle of partial conductances in mixtures.

[2] This value was obtained by taking the mean of the viscosities of the two 0.40 normal solutions.

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of the assumption that the relative mobilities of the K^+ and Cl^- ions are substantially the same in the mixture as in dilute potassium chloride solutions, this result shows that the principle is subject to serious inaccuracy, especially with respect to the effect upon the unibivalent salt, in the case of this mixture, which involves salts of two different types and a moderately high concentration (0.4 normal). This conclusion is justified even if errors are assumed as large as those mentioned above as possible (—0.001 in the value 0.289 and +0.005 in the value 0.504); for the value of the conductance ratio is then reduced only to 1.304, which is still 4.5 per cent. larger than the calculated value 1.248.

It is to be noted that, though the ratio of the actual partial conductances of the two salts is 7.5 per cent. larger than that required by the principle, yet the observed conductance of the mixture differs from the sum of the calculated partial conductances by only about 1 per cent., a result which is in accord with the previous tests of the principle which have been based upon conductance measurements alone.[1]

An examination of the partial conductance values in the second column of Table IV, which were calculated under the assumption that $\gamma = \Lambda/\Lambda_0$, without taking the influence of viscosity into account, shows that these agree fairly well (within 0.4 per cent. and 1.7 per cent.) with the partial conductances derived from the transference and conductance data. It seems, however, probable that this agreement is an accidental one, resulting from a compensation of the effect of the viscosity correction by that of a deviation from the principle of ionization in mixtures; for it seems almost certain that the ionization will be more accurately obtained when the change in viscosity of the medium is taken into account.

9. *Summary.*—In this article transference experiments made at 18° with a solution 0.2009 normal with respect both to potassium chloride and to potassium sulfate have been described. The quantity of chlorine transferred per faraday of electricity was found to be 0.289 ± 0.001 equivalent, this value being the mean of five results obtained by determining the changes in content at both the cathode and anode in three independent experiments.

Under the assumption that the transference number of the chlorine

[1] It may be mentioned that the principle that the ionization of each salt in the mixture is equal to that which it has when present alone at a concentration equivalent to the sum of the concentrations of the two salts leads to results which differ but little from those calculated by the principle considered above (according to whch it is the common ion concentration, rather than the total salt concentration, which determins the ionization). Thus the partial conductances calculated by the former principle under the assumption that $\gamma = \Lambda\eta/\Lambda_0\eta_0$ from the values Λ and η at 0.40 normal given in Table III are: $L_{KCl} = 0.02034$, and $L_{K_2SO_4} = 0.01663$. These will be seen to differ from those given in the third column of Table IV by only about 1 per cent.

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in the potassium chloride in this mixture is the same (0.504) as it is in dilute potassium chloride solutions, the proportion of the current carried by its ions was found to be 0.573, and the proportion carried by the ions of the potassium sulfate to be 0.427. By multiplying these values by the measured specific conductance of the mixture, the partial specific conductances of the two salts in the mixture were obtained.

The partial specific conductance of the potassium chloride so obtained was found to be 2.0 per cent. larger, and that of the potassium sulfate 5.2 per cent. smaller, than the values calculated by the principle, previously tested only by conductance measurements, that each salt in the mixture has an ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture, the ionization being taken equal to the ratio $\Lambda\eta/\Lambda_0\eta_0$, in which Λ and Λ_0 represent the equivalent conductances, and η and η_0 the viscosities, of solutions of the separate salts at the ion concentration in question and at zero concentration.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF IRON.

[THIRD PAPER.]

THE ANALYSIS OF FERROUS BROMIDE.

BY GREGORY PAUL BAXTER, THORBERGUR THORVALDSON AND VICTOR COBB.

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CONTENTS: 1. Introduction. 2. Purification of Materials. 3. Preparation of Ferrous Bromide for Analysis. 4. Method of Analysis. 5. Balance and Weighing.

1. Introduction.

The atomic weight of iron has already been subjected to two investigations in this laboratory. In one[1] ferric oxide was analyzed by reduction, in the other[2] the per cent. of bromine in ferrous bromide was determined. The first investigation yielded as a result 55.883 (O = 16.000), a value somewhat lower than the one in general use at the time, 56.0. The result of the second investigation, 55.871 (Ag = 107.93) confirmed so closely the value resulting from the oxide analysis, that, since the methods of the two investigations differ so radically, the matter was allowed to rest at this point until very recently. During the last few years much evidence has been brought forward to show that the older value for the atomic weight of silver, 107.93, is several hundredths of a unit too high and that the probable value lies at least as low as 107.88. With this lower value for silver and a correspondingly lower value for bromine the atomic weight of iron calculated from the bromide

[1] Richards and Baxter, *Proc. Am. Acad.*, 35, 253 (1900).

[2] Baxter, *Ibid.*, 39, 245 (1903).

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analyses is 55.845. The agreement of this corrected value with the result of the analysis of the oxide is far from satisfactory. It becomes imperative therefore to discover, if possible, the cause of the difficulty and to determin which of the early results is more reliable.

Neither of the methods mentioned above is entirely free from difficulties. In the oxide method, either the presence of magnetic oxide in the ferric oxide or incomplete reduction would have caused too high a result to be obtained. Since in the experiments by Richards and Baxter, the oxide was made from the nitrate by ignition in air, it is not easy to believe that an error from the first cause actually exists. On the other hand, very prolonged ignition at a high temperature in a current of hydrogen is necessary to insure even apparently complete reduction of ferric oxide to metal. Two indications of complete reduction were obtained by Richards and Baxter, one of which was constancy in the weight of the metal when repeatedly ignited in hydrogen, the other of which was complete solubility of the metal in dilute acid. Either of these tests might be misleading, however, since oxide might be so coated over with metal as to prevent or delay further reaction with the hydrogen, while it is well known that the solubility of ferric oxide in acid is increased by the presence of ferrous salts. It is true that gases occluded by the ferric oxide and released during reduction might have caused too great a loss in weight and hence have lowered the observed atomic weight of iron. But careful tests were made for occluded gases and no appreciable quantity was detected.

While the analysis of halogen salts for halogen has been found to be one of the most satisfactory methods of atomic weight determination, the analysis of ferrous bromide, as carried out by Baxter, was subject to a slight uncertainty. The bromide was made by sublimation in porcelain tubes and contained between one- and two-tenths of one per cent. of sodium bromide extracted from the tubes. The proportion of sodium bromide was unfortunately not as constant as could be desired, hence the correction which was applied for this impurity may be slightly in error.

On the whole, however, the ferrous bromide analysis seemed more satisfactory, and, since fused-quartz apparatus, which was not available for the earlier investigation, presented the possibility of many improvements in the preparation and analysis of the salt, it was decided, in taking up the subject anew, first to repeat the analysis of ferrous bromide.

2. Purification of Materials.

Water.—The ordinary distilled water of the laboratory was used in the preliminary stages of the purification of some of the materials used in this research, but for most purposes the laboratory supply was twice

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redistilled, first from alkaline permanganate, and then from very dilute sulfuric acid. Condensers of block tin were employed and rubber or cork connections were entirely avoided. In general, the water was collected in Jena glass flasks, but for special purposes either platinum or quartz receivers were used.

Nitric Acid.—Commercial C. P. nitric acid was purified by two distillations through a quartz condenser with the rejection of the first third of the distillate in each distillation. Nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is fairly pure. Here also quartz or platinum receivers were used whenever traces of alkalies were to be avoided.

Sulfuric Acid.—The best commercial article was distilled from a non-tubulated glass retort into an air-cooled flask. The first portion of the distillate was rejected. This acid was never used where a trace of alkali would have been harmful.

Ammonia.—Pure commercial ammonia of sp. gr. 0.90 was heated in a glass-stoppered boiling flask and the gas was absorbed in the purest water.

Solid Reagents.—Potassium permanganate, potassium dichromate, potassium and ammonium oxalates and oxalic acid were purified by several crystallizations from aqueous solution, with centrifugal drainage.

Silver.—The sample of silver used in this investigation was purified by methods which have been thoroughly tested in this laboratory.[1] Silver chloride was precipitated from strongly acid solution and after thorough washing by decantation, was reduced by means of sugar and sodium hydroxide. The metal was washed and fused upon charcoal before a blowpipe and the surface impurities were removed from the buttons by scrubbing with sea sand and etching with dilute nitric acid. The cleansed buttons were dissolved in nitric acid, and the solution, after neutralization, was precipitated with ammonium formate which had been prepared with distilled materials. Again the metal was thoroughly washed with water and fused with even more care than before in a porcelain crucible lined with the purest lime. The resulting buttons were in turn cleansed by etching with dilute nitric acid and were next converted into electrolytic crystals in a cell in which a concentrated, nearly neutral solution of silver nitrate served as electrolyte, and a pile of the buttons served as anode, the cathode being a stick of very pure silver from another preparation. After the crystals had been thoroughly washed with water, they were fused in a current of hydrogen in a porcelain boat lined with the purest lime. The boat was provided with cavities so that the buttons of silver varied considerably in size,

[1] See especially Richards and Wells, *Pub. Car. Inst.*, 28, 16 (1905); THIS JOURNAL, 27, 472.

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from 2 to 5 grams. The final product was freed from adhering lime by etching with dilute nitric acid and, after being washed with the purest water, it was dried, first in air at 100°, finally in a vacuum at about 500°.

A second sample was prepared in an exactly similar fashion by Dr. H. C. Chapin[1] for work upon the atomic weight of neodymium, except that it was necessary to cut the product into smaller fragments by means of a fine jeweler's saw. Surface contamination with iron from the saw was removed by etching with successive portions of dilute nitric acid until the acid remained free from iron. This specimen was used only in Analysis 13 and 27. Both specimens have already been used in a determination of the atomic weights of iodine and silver and have been found to give results identical with those of other very pure specimens of silver.[2]

Hydrobromic Acid.—This substance was prepared from bromine which had been carefully freed from chlorine and iodine by processes which have repeatedly been shown to be effective for the purpose in this laboratory. Commercial bromine was first distilled from solution in saturated aqueous potassium bromide. A portion of the product was next converted into potassium bromide by addition to a solution of twice recrystallized potassium oxalate, and the remainder of the bromine was distilled from solution in this potassium bromide, which must have been at any rate nearly free from chloride. Although in these two distillations from a bromide, the bromine must have been very effectually freed from chlorine, still another similar distillation was carried out later. The next step consisted in converting the bromine to hydrobromic acid. Hydrogen, made by the action of water on "hydrone," was purified and dried by scrubbing with water and passing over fused potassium hydroxide. This hydrogen was charged with a very nearly equivalent amount of bromine by bubbling through the latter substance at about 45° and the mixture was passed over hot platinized asbestos in a hard glass tube. The resulting hydrobromic acid was absorbed in the purest water. Needless to say, no cork or rubber connections were used in the apparatus for synthesizing hydrobromic acid except to connect the hydrogen generator to the purifying apparatus. In order to free the hydrobromic acid from iodine the solution was twice boiled for some time, after the addition of a small amount of the specimen of bromine which was used in the preparation of the acid, and finally with a small quantity of chlorine-free potassium permanganate. The hydrobromic acid solution was next distilled and then was converted into bromine by heating with a nearly equivalent amount of chlorine-free permanganate. In this way, since only five-eighths of the bromine is set free,

[1] *Proc. Am. Acad.*, 46, 213 (1910); THIS JOURNAL, 33, 16 (1911).
[2] Baxter, THIS JOURNAL, 32, 1591 (1910).

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the product received a third distillation from a bromide. The bromine was again converted into hydrobromic acid in the way already described, and the acid solution was freed from excess of free halogen by boiling and finally by distillation. Three different specimens of hydrobromic acid prepared in the same way, all gave identical results as far as could be determined.

Fuming hydrobromic acid was made by saturating the constant-boiling solution at 0° with hydrobromic acid gas synthesized as above. Especial care was taken to avoid an excess of bromine in the synthesizing apparatus.

Iron.—The preparation of pure iron has been discussed in the earlier papers upon the atomic weight of iron. Essentially the same methods were used in the purification of the three specimens employed in this investigation.

Sample A was made from very pure iron ribbon. After solution in redistilled nitric acid the ferric nitrate was three times crystallized from concentrated nitric acid with centrifugal drainage after each crystallization. All the operations, even the centrifugation, were performed in platinum vessels.

The nitrate was next dried and partially decomposed by heating on an electric stove in a platinum dish. The resulting mixture of oxide and basic nitrate was reduced to metal by means of ammonia, generated from a concentrated solution by means of solid sodium hydroxide and dried by the same substance. During the reduction, the oxide was contained in porcelain boats which were placed in a hard glass tube. Fused or ground connections were employed in the apparatus throughout. This sample of metal was used only for preliminary preparations.

Very pure metallic iron prepared by the American Rolling Mills Co. served as the starting point in the preparation of Sample B. It contained sulfur 0.019 per cent., phosphorus 0.003 per cent., carbon 0.018 per cent., silicon, trace, manganese, trace, copper 0.05 per cent.

In the purification of this material exactly the same course was followed as in the case of Sample A, except that the nitrate was crystallized five times from concentrated nitric acid, and the oxide was reduced in hydrogen, generated electrolytically from a solution of potassium hydroxide and dried by solid potassium hydroxide.

The purification of Sample C was even more thorough. The specimen of metal from the American Rolling Mills Co. was used here also. The block of iron, which was sawed from a larger piece, was washed first with ether, next with alcohol and finally with water. A superficial layer was then removed by etching with dilute nitric acid and the block was again washed with water. Upon dissolving the metal in

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redistilled hydrochloric acid, a small amount of insoluble matter remained, chiefly carbon in all probability. Without filtering, the solution was diluted with water and treated with hydrogen sulfide for some time, and a slight precipitate, consisting chiefly of sulfur and copper sulfide, was removed by filtration. On treating the solution twice more with hydrogen sulfide, only sulfur was precipitated. In this way all but traces of metals whose sulfides are insoluble in acids must have been eliminated.

In order to free the iron in particular from cobalt and nickel, it was next precipitated as ferric hydroxide by means of ammonia. First the ferrous chloride solution was oxidized by boiling for some time with a considerable amount of nitric acid, and after dilution it was poured, with continual agitation, into a hot solution of recrystallized ammonium nitrate containing a very large excess of redistilled ammonia. The precipitate was then washed many times by decantation. The process was next repeated, after dissolving the hydroxide in nitric acid. Preliminary experiments with iron containing known amounts of nickel showed that this method could be relied upon to remove traces of the latter element, although the complete elimination of large amounts is relatively slow. It is to be noted that, since the atomic weights of cobalt and nickel are so close to that of iron, the effect of a very considerable percentage of cobaltous or nickelous bromide in the ferrous bromide would be small.

The next step was to dissolve the ferric hydroxide in redistilled sulfuric acid and to reduce the iron electrolytically from the ferric to the ferrous state. This was done with a large platinum dish as cathode, and a platinum spiral of small surface as anode. The solution of ferric sulfate was concentrated in the first place, so that on cooling the reduced solution ferrous sulfate crystallized out. After removal of the crystals the electrolysis was continued and another crop of crystals obtained. By repeating these operations several times, almost all the iron was eventually recovered as ferrous sulfate. Metallic iron was then deposited electrolytically upon a platinum dish from a concentrated solution of recrystallized ammonium oxalate. During this electrolysis no manganese dioxide was deposited upon the anode, showing that the material was essentially free from this element. The metallic deposit was thoroughly washed with water and dissolved in the purest nitric acid. A small insoluble residue of carbon remained, which was removed by filtration through asbestos in a filtering apparatus consisting of only quartz and platinum. The asbestos had been digested for some time with aqua regia to remove soluble matter, and thoroughly washed with water. During the crystallization of the ferrous sulfate and the electrolytic deposition of the metal, aluminium and chromium as well as alkali metals

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and silica must have been eliminated. Further treatment of this specimen was exactly similar to that of Sample B.

Ferrous Bromide.—Ferrous bromide was made by dissolving the different preparations of pure iron in the constant-boiling solution of hydrobromic acid in a quartz dish. The acid was freshly distilled through a quartz condenser, and was collected in a quartz vessel. Although the reduction of the ferric oxide to metal was probably more or less incomplete, all three specimens of iron gave clear solutions. At first, the solution of the iron was carried on inside a large desiccator filled with very pure hydrogen, and by means of an electrical heater constructed with platinum wire inside the desiccator the solution was evaporated to crystallization. The crystals were rapidly removed from the solution and centrifugally drained in platinum Gooch crucibles. Although a portion of the material oxidized to ferric bromide in this operation, the large preponderance of ferrous salts effectually prevented solution of platinum. The crystals of ferrous bromide were then recrystallized in a similar manner from constant-boiling hydrobromic acid in a quartz dish, and after centrifugal drainage were preserved in a quartz dish in a desiccator containing sticks of potassium hydroxide. Sample A of ferrous bromide was prepared in this way from Sample A of iron.

Sample B of ferrous bromide was made from Sample B of iron in essentially the same way except that during the preparation of this sample it was found more convenient to dissolve the iron in hydrobromic acid in the air on an electric stove as rapidly as possible and to crystallize in the air. Although some oxidation unavoidably takes place, the greater portion of the ferric salt passes into the mother liquors. Since during the subsequent preparation of the ferrous bromide for weighing, all ferric salt is decomposed, slight oxidation is of no consequence. Sample B of ferrous bromide was three times crystallized from hydrobromic acid solution.

Sample C_1 of ferrous bromide was made from Sample C of iron in the same way and was crystallized five times from hydrobromic acid. Sample C_2 was obtained from the mother liquors of Sample C_1, after evaporation and reduction with metallic iron, and was crystallized five times. Sample C_3 resembled Sample C_1, except that the hydrobromic acid solution of ferrous bromide was filtered through asbestos in the platinum-quartz filtering tube, and then the salt was crystallized four times. The asbestos was digested with constant-boiling hydrobromic acid solution before use.

3. Preparation of Ferrous Bromide for Analysis.

As in the analysis of many other metallic bromides in this laboratory, the ferrous bromide was prepared for weighing by fusion in a current of nitrogen and hydrobromic acid gases. In the earlier work upon ferrous bromide

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fusion was unnecessary, since the salt was prepared by sublimation in a current of dry gases, and therefore contained only superficial moisture and ferric salt which could be eliminated by heating at a temperature below the fusing point. In the present instance, however, the salt contained at least four molecules of crystal water and possibly included ferric bromide. While in several recent investigations[1] it has been found possible to expel crystal water from hydrated crystals almost completely by heating them to a temperature at which they effloresce without melting, traces of moisture seem to be invariably retained. The desirability of fusing the ferrous bromide was therefore evident. Several difficulties were met in carrying out this operation. In the first place, in several preliminary experiments where the bromide was fused in a current of nitrogen and hydrobromic acid gases in a platinum boat, a superficial alloy of iron and platinum was formed. Whether this was due to dissociation of the salt or to the presence of a small proportion of hydrogen in the nitrogen was not determined. A similar difficulty met by Baxter and Coffin[2] in the fusion of cobaltous chloride in a current of pure hydrochloric acid gas leads one to believe that the former explanation is the real one. The only other material available for containing the salt during fusion was fused quartz. Fortunately experiments showed that ferrous bromide could be fused in a boat of this material in an atmosphere containing hydrobromic acid gas without attacking the quartz boat appreciably and without decomposition of the salt.

The second difficulty lay in the preparation of pure hydrobromic acid gas. In most previous investigations in this laboratory the method which has been used is to saturate nitrogen gas with bromine and then to pass the mixture through concentrated hydrobromic acid solution containing red phosphorus. Both before the hydrobromic acid solution becomes saturated with the gas and after a considerable amount of phosphorous acid has accumulated in the solution, volatil phosphorus compounds are likely to accompany the mixture of nitrogen and hydrobromic acid gases,[3] even if they are thoroughly scrubbed in a series of U-tubes containing saturated hydrobromic acid solution. This method was therefore used only in three of the preliminary experiments.

The method employed by Richards and Hönigschmid[4] in the fusion of calcium bromide, that of saturating hydrogen with bromine and passing it over hot platinum, is unsuited to the case of ferrous bromide on account of the occasional large excess of hydrogen in the hydrobromic acid gas.

[1] Baxter and Tilley, THIS JOURNAL, 31, 210 (1909). Baxter and Chapin, *Proc. Am. Acad.*, 46, 237 (1910); THIS JOURNAL, 33, 21.

[2] THIS JOURNAL, 28, 1584 (1906).

[3] Baxter, *Proc. Am. Acad.*, 39, 247 (1903).

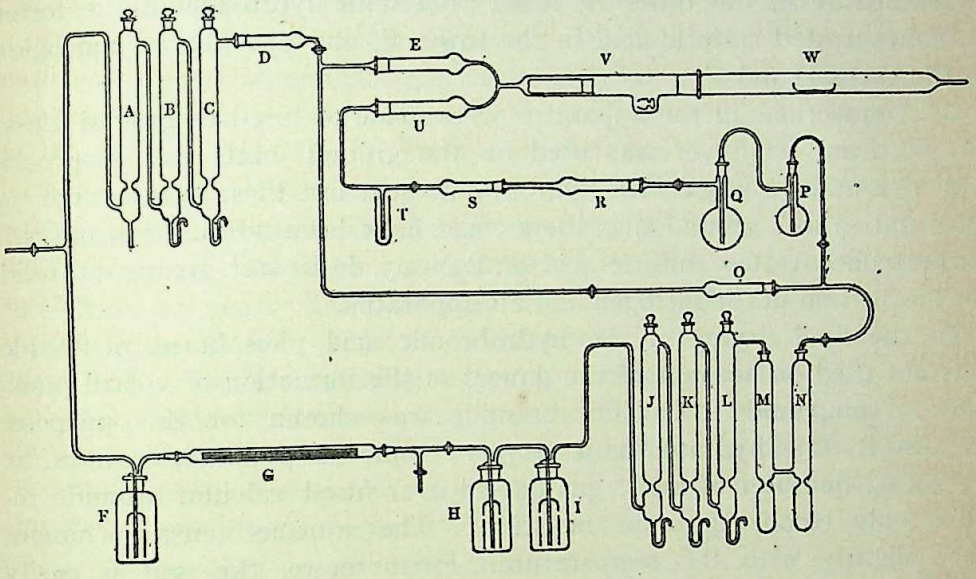
[4] THIS JOURNAL, 32, 1583 (1910).

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A more satisfactory method was found in charging the nitrogen with hydrobromic acid gas by passing it through fuming hydrobromic acid solution. In this way all possibility of contamination with phosphorus was avoided.

The apparatus for preparing the various gases was as follows: Nitrogen was obtained by passing air through concentrated ammonia solution in the bottle F (see figure) and then over hot copper gauze in the hard-



glass tube G. The excess of ammonia was removed by dilute sulfuric acid in the bottles H and I. The gas was then conducted through a tower, J, filled with beads moistened with silver nitrate solution, two similar towers, K and L, containing dilute sulfuric acid to eliminate last traces of ammonia, and two towers, M and N, filled with sticks of fused potassium hydroxide to absorb carbon dioxide and moisture. In the first three experiments the partially dried gas, after bubbling through bromine in a small flask, passed into a second flask containing concentrated hydrobromic acid solution in which carefully washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid solution, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes, containing beads moistened with concentrated hydrobromic acid solution only, served to eliminate volatil phosphorus compounds. Finally the mixture of nitrogen and hydrobromic acid gases was thoroughly dried by means of fused calcium bromide.

In all except the first three experiments the nitrogen was charged with hydrobromic acid gas by bubbling through fuming hydrobromic acid solution in the bulbs P and Q. The mixture was dried by means of fused calcium bromide in the tube R, and, after being freed from a possible

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trace of bromine by anhydrous ferrous bromide in the tube S, was passed a second time over fused calcium bromide in the tube U. The fuming hydrobromic acid solution contained ferrous bromide to prevent the evolution of bromine.

When desired, the nitrogen could be passed directly through the phosphorus pentoxide tubes, O and E, into the bottling apparatus VW in which the fusion took place. Air was purified and dried by passing over silver nitrate in the tower A, fused potassium hydroxide in the tower B, concentrated sulfuric acid in the tower C, and phosphorus pentoxide in the tubes D and E.

All connections in the apparatus were made of fused or ground glass. No lubricant whatever was used on the ground joints and stopcocks which came in contact with hydrobromic acid but these joints were so long and so well ground that there could have been no diffusion inward. Either concentrated sulfuric acid or Ramsay desiccator grease was used for lubrication in the nitrogen and air apparatus.

In the final drying of the hydrobromic acid phosphorus pentoxide was not used on account of the danger of the formation of volatil phosphorus compounds.[1] Calcium bromide was chosen for this purpose, because its first hydrate has a very low aqueous pressure, 0.2 mm. at 25°, *i. e.*, one liter of moist gas passed over fused calcium bromide retains only 0.0002 gram of moisture.[2] The aqueous tension changes very slightly with the temperature. Furthermore, this salt is easily prepared. Fused zinc bromide is a less efficient drying agent. The aqueous pressure of its lowest hydrate is 1.2 mm. at 25°, and increases rather rapidly with the temperature.[3]

The ferrous bromide contained in the weighed quartz boat was placed in the heating tube W of the bottling apparatus,[4] and after air had been expelled by nitrogen and then by a mixture of nitrogen and hydrobromic acid gases, the tube was gradually heated until the water of crystallization began to evaporate rapidly.[5] There was never any appearance of melting at this point. As soon as dehydration appeared to be complete, the temperature was still further raised until the ferrous bromide fused. The salt was allowed to solidify, and while cooling, the mixture of nitrogen and hydrobromic acid gases was replaced by nitrogen, and this in turn by dry air when the tube was cold. While the tube was being swept out with nitrogen and air, a portion of the current of gas was sent backward through the tube U and the trap T, in order to avoid

[1] Baxter, Hines and Frevert, THIS JOURNAL, 28, 779 (1906).

[2] From results by Baxter and Warren, published in this number of THIS JOURNAL, p. 342.

[3] *Ibid.*

[4] Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

[5] At about 200°, Dammer, *Handb. anorg. Chem.*, 4, 761.

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all possibility of contamination with hydrobromic acid. Finally the boat was pushed into the weighing bottle contained in the socket of V the bottling apparatus, and the stopper was inserted, all in the current of pure dry air. Several hours' standing in a desiccator near the balance always preceded the weighing of the bottle with its contents. In the preliminary series of experiments the fusion tube was of hard glass but in the final series of experiments this was replaced by a tube of transparent fused quartz. This quartz tube remained essentially unattacked during the final series of experiments. The tube was electrically heated by means of a removable mica sleeve wound with "Nichrome" resistance ribbon.

4. Method of Analysis.

The procedure for the determination of the bromine in ferrous bromide was essentially that already frequently employed in the analysis of bromides in this laboratory. A solution of the salt was titrated against a weighed very nearly equivalent amount of silver and then the precipitated silver bromide was collected and determined gravimetrically. However, owing to the reducing effect of ferrous solutions upon solutions of silver salts, preliminary oxidation of the ferrous iron to the ferric state was found necessary in the earlier research upon ferrous bromide.

The salt was dissolved in about 200 cc. of pure water containing two drops of redistilled sulfuric acid. The acid was necessary, since ferrous bromide dissolved in pure water alone oxidizes rapidly and gives a copious precipitate of basic salt. After dilution to at least 600 cc. in a three-liter glass-stoppered precipitating flask, a solution was added containing ninety-nine per cent. of the amount of thrice crystallized potassium dichromate necessary to complete the oxidation and five per cent. more than the theoretical amount of distilled sulfuric acid. In order to avoid loss of bromine by evaporation from the surface of the solution, the dichromate was introduced through a funnel with a fine tip reaching to the bottom of the liquid. The solutions were allowed to mix largely by diffusion, aided by occasional very gentle agitation, and the flask was kept closed for some time after the introduction of the dichromate. When the oxidation is effected in this way, absolutely no evidence of free bromine can be obtained in the atmosphere above the solution, although we found experimentally that less than 0.01 mg. of bromine could easily be detected by the odor in an empty three-liter flask.

Very nearly the exact amount of the purest silver to combine with the ferrous bromide was weighed out and dissolved in redistilled nitric acid which had been diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible spatterings. The solution was further diluted and heated until free from nitrous acid, and then was again diluted until not more concentrated than tenth-nor-

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mal. This solution was next added to the ferrous bromide solution which also had been diluted until more dilute than tenth-normal. After thorough mixing by shaking, the flask with its contents was allowed to stand for several days with occassional shaking until the supernatant liquid seemed perfectly clear. The solution was then tested for an excess of bromide or silver in a nephelometer[1] with careful observance of all the precautions necessary in the use of this instrument. If a deficiency in either bromide or silver was observed, a suitable amount of a thousandth-normal solution of sodium bromide or silver nitrate was added and the shaking and testing were repeated. This process was continued until the amounts of bromide and silver were equivalent. The test portions, since they contained only negligible amounts of silver and bromine, were discarded.

In order to determin whether appreciable occlusion had taken place, in Analyses 9 and 25, and 13 and 27, the precipitates were allowed to stand in contact with their mother liquors for 3 and 2 weeks respectively after the end point had apparently been reached. No change in end point with the time could be detected. In Analyses 13 and 27, moreover, the precipitation was carried out in the reverse fashion by adding the bromide solution to the silver solution. The results of these analyses were no different from those of the others. Further evidence that no occlusion took place is furnished by the ratio of silver to silver bromide (see page 333).

After the exact end point had been reached in each analysis, an excess of about 6 centigrams of silver nitrate was added and the flask was again thoroughly shaken. When the supernatant liquid was clear, the precipitate was thoroughly washed with pure water and collected upon a Gooch-Munroe-Neubauer crucible which had been heated to constant weight at 170° in an electric oven. The crucible and contents were heated for about 15 hours at the same temperature in the electric oven before being weighed. The greater part of the silver bromide was transferred to a porcelain crucible and the residual moisture was estimated by determining the loss in weight upon fusion. With two excepions the fused silver bromide was light yellow and transparent. In these two analyses red particles of some iron compound were visible in the bromide and the results of these analyses were lower than those of the others. These two analyses are omitted from the table of results.

The precipitating flask was carefully rinsed with ammonia, and the silver bromide content of the solution was compared nephelometrically with known bromide solutions. The quantity found in this way was always less than one-tenth of a milligram.

While silver bromide is essentially insoluble in a solution containing

[1] Richards and Wells, *Am. Chem. J.*, 31, 235 (1904); 35, 510 (1906).

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a bromide or a silver salt, it dissolves slightly in pure water. The first few washings, owing to the excess of silver nitrate in the filtrate, undoubtedly did not dissolve an appreciable amount of the bromide. Even the later washings, amounting to about one liter, could hardly have become saturated with bromide. The correction actually applied in each analysis for solubility of the silver bromide, 0.0001 gram per liter, certainly can not be far from the correct one.[1]

5. Balance and Weighing.

All the weighings were performed in a Troemner balance No. 10, easily sensitive to 0.02 milligram. The gold-plated brass weights were standardized from time to time by the method described by Richards.[2] No changes of more than a few hundredths of a milligram were found, however. Variations in the weights of containing vessels owing to changing atmospheric conditions were avoided by using counterpoises of the same material and as nearly as possible of the same shape and volume. The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction.
Weights	8.3[3]	....
Silver	10.49[4]	— 0.000031
Silver bromide	6.473[5]	+ 0.000041
Ferrous bromide	4.636[6]	+ 0.000114

In the following tables are given the results of all the analyses completed, except three which met with known mishaps. The analytical work was performed wholly by Mr. Thorvaldson.

ATOMIC WEIGHT OF IRON.

Ag = 107.88. Br = 79.916.

Preliminary Series I. $FeBr_2$: 2Ag.

Number of analysis.	Sample of $FeBr_2$.	Weight of $FeBr_2$ in vacuum. Grams.	Weight of Ag. in vacuum. Grams.	Weight of Ag added. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $FeBr_2$: 2 Ag.	Atomic weight of iron.
1	A	3.45339	3.45441	0.00040	3.45481	0.999589	55.840
2	A	3.04933	3.05030	0.00025	3.05055	0.999600	55.841
3	A	2.9007	2.9018	0.0001	2.9019	0.999586	55.839
4	B	3.0873	3.0884	0.0001	3.0885	0.999611	55.844
5	B	3.50278	3.50416	0.00010	3.50426	0.999577	55.837
6	B	4.05239	4.05379	0.00025	4.05404	0.999593	55.840
7	B	4.08516	4.08653	0.00030	4.08683	0.999593	55.840
					Average,	0.999593	55.840

[1] Böttger finds the solubility to be 0.00008 g. per liter at 20°, *Z. physik. Chem.*, 46, 602 (1903). Kohlrausch gives the value 0.00011 at 21°, *Ibid.*, 50, 356 (1905).

[2] THIS JOURNAL, 22, 144 (1900).

[3] Baxter, *Proc. Am. Acad.*, 42, 209 (1906); THIS JOURNAL, 28, 1321.

[4] Richards and Wells, *Pub. Car. Inst.*, 28, 11 (1905); THIS JOURNAL, 27, 466.

[5] Baxter and Hines, *Am. Chem. J.*, 31, 224 (1904).

[6] Baxter, *Proc. Am. Acad.*, 39, 251 (1903).

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FINAL SERIES I. $FeBr_2$: 2Ag.

Number of analysis.	Sample of $FeBr_2$.	Weight of $FeBr_2$ in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $FeBr_2$: 2 Ag.	Atomic weight of iron.
8	B	5.03555	5.03769	0.00005	5.03774	0.999565	55.834
9	C_2	6.06309	6.06557	0.00000	6.06557	0.999592	55.840
10	C_2	5.59258	5.59492	—0.00010	5.59482	0.999599	55.842
11	C_1	5.89767	5.90014	0.00000	5.90014	0.999581	55.838
12	C_1	4.48546	4.48732	0.00010	4.48742	0.999563	55.834
13	B	5.41562	5.41794	0.00005	5.41799	0.999563	55.834
14	A	6.50002	6.50272	0.00005	6.50277	0.999577	55.837
15	C_1	3.56564	3.56719	0.00000	3.56719	0.999565	55.834
16	B	5.32434	5.32662	—0.00020	5.32642	0.999609	55.844
17	C_3	6.38845	6.39124	—0.00030	6.39094	0.999610	55.844
18	C_3	6.37952	6.38223	—0.00010	6.38213	0.999591	55.840
	Total,	60.64794			60.67313	0.999585	55.838
					Average,	0.999583	55.838

ATOMIC WEIGHT OF IRON.

Ag = 107.880. Br = 79.916.

Preliminary Series II. $FeBr_2$: 2AgBr.

Number of analysis.	Sample of $FeBr_2$.	Weight of $FeBr_2$ in vacuum. Grams	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $FeBr_2$: 2 AgBr.	Atomic weight of iron.
19	A	3.45339	6.01412	0.00054	6.01358	0.574265	55.853
20	A	3.04933	5.31057	0.00028	5.31029	0.574228	55.844
21	B	3.50278	6.10048	0.00015	6.10033	0.574195	55.831
22	B	4.05239	7.05799	0.00047	7.05752	0.574195	55.831
						0.574221	55.840

FINAL SERIES II. $FeBr_2$: 2AgBr.

Number of analysis.	Sample of $FeBr_2$.	Weight of $FeBr_2$ in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $FeBr_2$: 2AgBr.	Atomic weight of iron.
23	B	5.03555	8.76960	0.00010	8.76950	0.574212	55.837
24	C_2	6.06309	10.55911	0.00022	10.55889	0.574216	55.839
25	C_2	5.59258	9.73988	0.00014	9.73974	0.574202	55.834
26	C_1	5.89767	10.27065	0.00008	10.27057	0.574230	55.844
27	B	5.41562	9.43199	0.00028	9.43171	0.574193	55.830
28	A	6.50002	11.31990	0.00032	11.31958	0.574227	55.843
29	C_1	3.56564	6.21000	0.00013	6.20987	0.574189	55.829
30	B	5.32433	9.27263	0.00026	9.27237	0.574216	55.839
31	C_3	8.51818	14.83494	0.00026	14.83468	0.574207	55.836
32	C_3	6.38845	11.12550	0.00014	11.12536	0.574224	55.842
33	C_3	6.37952	11.11011	0.00040	11.10971	0.574229	55.844
	Total,	64.68065			112.64198	0.574214	55.838
					Average,	0.574213	55.838

Average of Final Series I and II, 55.838.

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In seeking to discover the most probable value for the atomic weight of iron indicated by the foregoing data, it is only fair to bear in mind that the first experiments of a series are almost invariably influenced by incidental experimental errors which are largely eliminated in later experiments. Furthermore, the first three samples of ferrous bromide to be analyzed were fused in hydrobromic acid prepared from bromine and red phosphorus and hence, may have contained traces of phosphorus, while a hard glass tube was used in the fusion of the next four samples. We have therefore collected in the two preliminary series the first seven analyses, made in the summer and fall of 1909. The two final series were completed during the winter of 1909–10 after a very considerable intermission and are, in our opinion, much more satisfactory and less subject to avoidable errors.

The averages of the two final series agree perfectly, showing that so far as the estimation of the bromine is concerned no serious constant error exists. This is further indicated in the following table where the ratio of silver used and silver bromide obtained in the different pairs of analyses is recorded.

	Preliminary.	Ag : AgBr.
Analyses	1 and 19	0.574502
	2 and 20	0.574460
	5 and 21	0.574438
	6 and 22	0.574428
	Average,	0.574457
	Final.	
	8 and 23	0.574461
	9 and 24	0.574451
	10 and 25	0.574432
	11 and 26	0.574471
	13 and 27	0.574444
	14 and 28	0.574471
	15 and 29	0.574439
	16 and 30	0.574440
	17 and 32	0.574448
	18 and 33	0.574464
	Average,	0.574452

The average ratio agrees with the value to be expected, 0.574453.[1]

The different samples of ferrous bromide appear to be exactly similar as far as can be told by the results of the analyses. The following table contains a comparison of the averages from the different samples in the final series.

[1] Baxter, *Proc. Am. Acad.*, **42**, 210 (1906); THIS JOURNAL, 28, 1332.

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Sample.	$FeBr_2 : 2Ag$.	$FeBr_2 : 2AgBr$.	Average.
A	55.837	55.843	55.840
B	55.837	55.835	55.836
C	55.839	55.838	55.839
Average,	55.838	55.839	55.838

In the final series 60.64794 grams of ferrous bromide combined with 60.67313 grams of silver, whence the atomic weight of iron is 55.838, while 64.68065 grams of ferrous bromide produced 112.64198 grams of silver bromide, the amount to be expected if the atomic weight of iron is 55.838.

No matter how the results are treated, the outcome is the same. This method indicates a value for the atomic weight of iron of 55.838 if silver is taken as 107.88.

Certain possible constant errors need to be discussed. In two analyses of ferrous bromide prepared from meteoric iron, described in the following paper in the atomic weight of meteoric iron, the oxidation of the ferrous bromide to the ferric state before the precipitation of the silver bromide was carried out with ninety-eight instead of ninety-nine per cent. of the theoretical dichromate necessary. These two analyses yielded results very slightly lower than analyses with similar material in which ninety-nine per cent. of the theoretical dichromate was used, owing possibly to reduction of silver salts by the residual ferrous salt. The question naturally arises whether ninety-nine per cent. of dichromate is enough to prevent reduction of silver salts. In this connection it must be remembered that the ferrous salt was from the moment of solution undergoing continual oxidation, and that in reality less than one per cent. remained unoxidized after the addition of the dichromate. As the solution was always allowed to stand several hours after the addition of the dichromate, before precipitation, this oxidation must have been very considerable. Secondly, the average ratio of silver used to silver bromide obtained has exactly the proper value, which indicates that the silver bromide contained no excess of silver. This point is substantiated by the appearance of the fused silver bromide, which, as has already been stated, was light yellow and transparent. Furthermore, the reducing effect of ferrous salts on silver salts diminishes with the concentration of both substances. For instance, while a 0.5 per cent. acid solution of ferrous sulfate gave a precipitate of silver with an equal amount of a 0.06 per cent. solution of silver nitrate on standing over night, the same ferrous solution gave no precipitate with a 0.03 per cent. solution of silver nitrate. Similarly a 0.1 per cent. solution of ferrous sulfate gave no precipitate with even a 20 per cent. solution of silver nitrate. Since in an analysis the concentration of silver nitrate used

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in precipitation was never over one per cent., while, if one per cent. of the ferrous bromide was unoxidized, the concentration of the latter substance could never have been higher than 0.003 per cent., the possibility of reduction was certainly small.

Although one of us[1] has already shown that it is possible to free ferrous bromide from ferric salt by heating in a current of nitrogen and hydrobromic acid gases to about 400°, the experiment for the detection of ferric salt was repeated with the fused ferrous bromide. The salt fused as described above was transferred to the weighing bottle in an atmosphere of nitrogen. The stopper of the weighing bottle was then removed and a freshly boiled and cooled, slightly acid solution of ammonium thiocyanate was quickly poured into the bottle, completely filling the bottle. The bottle was again stoppered and allowed to stand until the ferrous bromide was dissolved. Although the solution did not remain perfectly colorless, the color of the ferric thiocyanate was not strong. By comparison with solutions of known amounts of ferric iron the quantity of ferric bromide was found to be less than 0.05 milligram. So slight an amount of oxidation as this might well have occurred during the solution of the salt. At any rate it is obviously unnecessary to apply a correction of this magnitude.

The question of the neutrality of the ferrous bromide is difficult to settle, in particular because a basic precipitate is formed by oxidation as soon as the salt is dissolved in water. In many similar instances, however, where metallic bromides have been fused and allowed to solidify in hydrobromic acid gas, the salts have been found to be essentially neutral, hence it is fair to assume that this is the case with ferrous bromide also, especially since the concentration of the hydrobromic acid gas was never very high during the fusion. Furthermore, if the salt was not neutral, such variations in the method of heating and fusing as actually occurred would be expected to produce variations in the basicity or acidity of the salt. That such variations were inappreciable is indicated by the agreement of the different results.

None of the specimens of fused ferrous bromide gave a perfectly clear solution, even when dissolved in water containing considerable acid. The insoluble substance consisted of a trace of black material, undoubtedly carbon, since it disappeared when collected on a filter and ignited, and a very small amount of a light colored precipitate visible only under the most favorable conditions. The quantity of both kinds of material varied somewhat in different fusions and in the most successful experiments the insoluble material was almost entirely absent. Variations in the manner and speed of heating the ferrous bromide seemed to have no perceptible effect on the quality of the fused material.

[1] Baxter, *Proc. Am. Acad.*, 39, 246 (1903).

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Finally the attempt was made to determin the weight and composition of the residue. Acidified solutions of fused ferrous bromide were filtered through tiny filters, and the papers were thoroughly washed. The filtrates seemed perfectly clear. The filters were ignited and the residues weighed in platinum crucibles. Since many salts of heavy metals are adsorbed from solution by filter paper,[1] blank experiments were carried out by filtering again the once filtered solutions. In four experiments the residues obtained from the original material weighed 0.30, 0.14, 0.15, and 0.12 milligram, while three blank experiments yielded 0.13, 0.13 and 0.12 milligram of ignited residue. The four residues were boiled with aqua regia, and the solution was evaporated. The solution was found to contain a trace of iron, while a slight insoluble gray residue which appeared to be silica remained. Whatever the composition of the residue, its weight is insignificant. If the residue was silica, it may have been extracted from the quartz boat which lost in weight at the rate of a few hundredths of a milligram in each analysis.

The uncertainty introduced by the last three considerations is not large enough to affect the second decimal place in the atomic weight of iron. The rounded-off value 55.84 confirms the earlier work on ferrous bromide as closely as could be expected while the greater purity of the ferrous bromide which we prepared gives greater probability to the result of this research than to that of the earlier one on the bromide. Since the bromide method of atomic weight investigation has been thoroughly tested with numerous metallic bromides, the results of this investigation are entitled to greater weight than the earlier results from the analysis of ferric oxide. Until the opportunity is offered for investigating farther the analysis of ferric oxide, it seems decidedly safer to employ the lower value for the atomic weight of iron yielded by the analysis of ferrous bromide.

In the following paper is described a continuation of this research by the determination of the atomic weight of meteoric iron.

We are particularly indebted to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

Following is a summary of the chief results of this investigation:

1. A new method of preparing very pure ferrous bromide is described.

2. The analysis of this salt indicates that the atomic weight of iron is 55.838 referred to silver 107.880. If silver is assumed to have the atomic weight 107.870, iron becomes 55.833.

CAMBRIDGE, MASS.

[1] Baxter and Hines, THIS JOURNAL, 28, 1569 (1906). Baxter and Wilson, *Proc. Am. Acad.*, 43, 369 (1907); THIS JOURNAL, 30, 191.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF IRON.

[FOURTH PAPER.]

THE ATOMIC WEIGHT OF METEORIC IRON.

BY GREGORY PAUL BAXTER AND THORBERGUR THORVALDSON.

Received January 18, 1911.

So far as we know atomic weight investigations have always in the past been carried out with material of terrestrial origin. While there is no reason to believe that an extra-terrestrial element differs from the corresponding terrestrial element in any way, a comparison is at any rate worth while.[1] As sensitive a means as any other for detecting a difference between the two sorts of material lies in the determination of the atomic weight, and since iron is one of the few elements available in sufficient amount for such a comparison, at the close of the research upon the atomic weight of iron described in the preceding paper the experiments were continued with meteoric material.

Through the kindness of Professor John Eliot Wolff, Curator of the Mineralogical Museum of Harvard University, we were fortunate enough to secure a considerable quantity of the "Cumpas" meteorite weighing 63 pounds, found in 1903 near Cumpas, Sonora, Mexico. The meteorite shows well-marked Widmanstättian figures on etching with nitric acid. The sample given us contained a little over 88 per cent. of iron, the chief impurity being nickel.

In general the separation of the iron from the accompanying impurities and the determination of the atomic weight by analysis of ferrous bromide followed the course outlined in the preceding paper. The original turnings of meteorite were dissolved in hydrochloric acid, and an insoluble residue which remained was removed by filtration. Upon saturating the solution with hydrogen sulfide, apparently no precipitate except sulfur was formed. The solution was then made nearly neutral by the addition of ammonia, and was again saturated with hydrogen sulfide. The resulting small amount of black precipitate, chiefly ferrous sulfide, was collected upon a filter and rejected. Next an excess of ammonia was added, hydrogen sulfide was passed in until precipitation was complete, and the precipitated sulfides were thoroughly washed by decantation. Upon treating the sulfides with 4 per cent. hydrochloric acid solution the greater part of the nickel and cobalt sulfides remained insoluble. After filtration the process of precipitating the ferrous sulfide and redissolving in dilute hydrochloric acid was repeated. The second residue of nickel and cobalt sulfides was so small that it seemed advisable to re-

[1] Such a comparison was suggested to one of us nearly ten years ago by Prof. T. W. Richards, and independently through him more recently by Sir Henry Roscoe.

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move the remainder of the nickel and cobalt by precipitating the iron as ferric hydroxide in the presence of large amounts of ammonium salts and ammonia. First the ferrous chloride solution was oxidized by boiling with nitric acid, and then, after dilution, it was poured into a large volume of redistilled ammonia. The mother liquor of this precipitation, when evaporated to small bulk and treated with ammonium sulfide, was found to contain nickel, hence the precipitate of ferric hydroxide, after being washed by decantation, was dissolved in nitric acid and reprecipitated with ammonia as before. In all, nine such precipitations were necessary to eliminate the nickel and cobalt completely. The ninth precipitate of ferric hydroxide was dissolved in redistilled sulfuric acid and was converted into ferrous bromide exactly as described in the preceding paper with Sample C, by electrolytic reduction and crystallization as ferrous sulfate, electrolytic deposition as metal from oxalate solution, solution in nitric acid and crystallization as ferric nitrate, ignition to oxide, reduction in hydrogen, and solution in concentrated hydrobromic acid solution and crystallization as ferrous bromide. On account of the limited quantity of material, in the crystallizations of the ferric nitrate and the ferrous bromide the mother liquors were worked up by the usual process of fractional crystallization. During the purification of this material no difference in behavior could be discerned from that of terrestrial iron.

The ferrous bromide was prepared for analysis by dehydration and fusion in a current of dry nitrogen and hydrobromic acid gases, in a quartz boat contained in a quartz tube. After being weighed it was dissolved in acidulated water and oxidized to the ferric state by dichromate. Finally the bromine was determined by titration against silver and the silver bromide was estimated gravimetrically. The details of the procedure were exactly as described in the preceding paper. Sufficient material for only five analyses was finally obtained.

ATOMIC WEIGHT OF IRON.

Ag = 107.880. Br = 79.916.

Series I. $FeBr_2 : 2Ag$

Number of analysis	Weight of $FeBr_2$ in vacuum. Grams.	Weight of Ag. in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $FeBr_2 : 2Ag$.	Atomic weight of iron.
1	3.95460	3.95621	0.00010	3.95631	0.999568	55.835
2	4.66954	4.67147	0.00030	4.67177	0.999523	55.825
3	4.75335	4.75530	0.00020	4.75550	0.999548	55.831
4	6.95582	6.95894	—0.00040	6.95854	0.999609	55.844
5	3.20762	3.20864	0.00040	3.20904	0.999557	55.833
				Average,	0.999561	55.834
				Average, rejecting Nos. 2 and 3,	0.999578	55.837

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Series II. $FeBr_2$: 2AgBr.

Number of analysis.	Weight of $FeBr_2$ in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $FeBr_2$: 2 Ag.	Atomic weight of iron.
6	3.95460	6.88729	0.00009	6.88720	0.574196	55.831
7	4.66954	8.13307	0.00025	8.13282	0.574160	55.818
8	4.75335	8.27870	0.00015	8.27855	0.574177	55.824
9	6.95582	12.11361	0.00032	12.11329	0.574230	55.844
10	3.20762	5.58655	0.00023	5.58632	0.574192	55.830
				Average,	0.574191	55.829
				Average, rejecting Nos. 7 and 8,	0.574206	55.835

While the average of the two series, 55.832, is slightly lower than the outcome of the work described in the preceding paper, 55.838, the difference corresponds to only one part in ten thousand in the atomic weight of iron and to less than one part in thirty thousand in the molecular weight of ferrous bromide, the quantity actually determined. It is to be noted that analyses 4 and 9, in which the largest amount of material was used, gave a result even higher than the average of the preceding series. In the four lowest analyses 2 and 7, and 3 and 8, a modification was introduced in the method of analysis, which consisted in adding 98 instead of 99 per cent. of the dichromate necessary to oxidize the ferrous salt. In one of these analyses the fused silver bromide, instead of being yellow, was perceptibly darker than the pure substance, possibly owing to slight reduction of the silver salts by the unoxidized ferrous salt. The ratio of silver to silver bromide in these four experiments is distinctly lower than the value to be expected, 0.574453.[1]

		Ag : AgBr.
Analyses	1 and 6	0.574444
	2 and 7	0.574434
	3 and 8	0.574436
	4 and 9	0.574455
	5 and 10	0.574446

In the preceding paper the conclusion was reached that 99 per cent. of the dichromate theoretically necessary is sufficient to avoid error from reduction. If the four experiments giving the lowest ratio of silver to silver bromide, 2 and 7 and 3 and 8, are omitted, the averages of the two series become 55.837 and 55.835 respectively, which agree as closely with the final result of the preceding investigation as can be expected. Even the average of the four experiments in question differs from that of the others by only one part in twenty thousand in the molecular weight of ferrous bromide. At any rate there seems to be no evidence of dissimilarity between this specimen of meteoric iron and the ordinary metal. We intend to investigate this problem farther.

[1] Baxter, *Proc. Am. Acad.*, 42, 210 (1906); THIS JOURNAL, 28, 1332.

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We are particularly indebted to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE EFFICIENCY OF CALCIUM BROMIDE, ZINC BROMIDE AND ZINC CHLORIDE AS DRYING AGENTS.

BY G. P. BAXTER AND R. D. WARREN.

Received January 18, 1911.

The problem of the drying of hydrobromic acid gas is one which has frequently been met in this laboratory in the preparation of anhydrous metallic bromides for analysis. Until recently phosphorus pentoxide was used as the final drying agent, but experiments by Baxter and Hines[1] in the drying of hydrochloric acid gas with phosphorus pentoxide have shown that the pentoxide is attacked by the acid gas with the formation of volatil phosphorus compounds, and that therefore there is danger in using this drying agent for hydrobromic acid also. Since hydrobromic acid gas is decomposed by concentrated sulfuric acid, fused metallic bromides seemed to be the most suitable substances for the desiccation of this gas. Hence experiments were carried out with two anhydrous bromides which can easily be prepared in a state of sufficient purity, with the purpose of determining their efficiency as drying agents.

Since phosphorus pentoxide was used to absorb the residual moisture in the gas which had been exposed to the anhydrous bromides, it was not possible to employ hydrobromic acid as the gas to be dried. Instead air was used for this purpose, since the nature of the gas is of no consequence, provided the gas does not combine with the drying agent.

The method was as follows: A measured amount of moist air was passed through a tube containing a layer of crushed fused bromide, and then through a weighed phosphorus pentoxide tube. From the gain in weight of the pentoxide tube and the volume of air passed through the system, the pressure of the aqueous vapor in the air which was in equilibrium with the fused bromide could be determined.

The calcium bromide was made from very pure calcium carbonate which had been precipitated from a solution of the nitrate, and a solution of hydrobromic acid which had been synthesized from pure bromine and hydrogen. The bromine had been twice distilled from a bromide so that it must have been free from chlorine. The slightly acid solution of the bromide was evaporated in a platinum dish, and the residue was

[1] THIS JOURNAL, 28, 779 (1906).

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fused. The mass was next broken into small pieces, and transferred to the drying tube.

The drying tube consisted of a U-tube with arms about 25 cm. in length and about 15 mm. in diameter. About 30 mm. of this tube was filled with the anhydrous bromide. The air was purified and partially dried by passing through a tower filled with beads moistened with a concentrated potassium hydroxide solution. After passing through the tube containing calcium bromide, the air was conducted into a weighed glass-stoppered U-tube containing phosphorus pentoxide which had been resublimed in a current of oxygen. Beyond the weighed phosphorus pentoxide tube was placed a second pentoxide tube to prevent back diffusion of moisture. The current of air was produced by means of an 8-liter aspirator bottle, provided with a thermometer for determining the temperature of the air at the end of the experiment, an open-tube manometer filled with water, and a siphon tube. Fused or ground glass joints were used in the system as far as the weighed phosphorus pentoxide tube.

During an experiment the portion of the tube containing the calcium bromide was immersed in a water thermostat, the temperature of which was kept constant within 0.1°. The pentoxide tube was weighed by comparison with a counterpoise of very nearly equal size, shape, and weight, one stopcock of each tube being open during the weighing. The volume of air passed through the system was determined by measuring the water delivered by the siphon tube from the aspirator bottle.

In each experiment the weighed phosphorus pentoxide tube was attached in place by short, tightly fitting rubber connections and about 8 liters of air were passed through the system. The phosphorus pentoxide tube was then reweighed. From the weight of water was calculated its volume under standard conditions. The volume of air passed through the system was corrected to standard conditions, dry, and the proportion of water vapor by volume was found by dividing the volume of the water vapor by the sum of the volumes of the water and dry air. The pressure of the water vapor was found by multiplying the internal pressure of the system, as determined from the barometric reading and the reading of the manometer in the aspirator bottle, by the proportion of water by volume.

The experiments were varied by passing air which had been previously dried with phosphorus pentoxide through the calcium bromide tube, after the first portions of the calcium bromide had been allowed to take up moisture in the experiments carried out as described above. In this way equilibrium was approached from the opposit direction.

Furthermore, in order to determin whether the drying or saturation of the gas was efficient and whether the absorption of the water in the pentoxide tube was complete, the rate at which the air was passed through

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the calcium bromide tube was varied from 1 liter per hour to 1 liter per quarter hour. These variations were without very marked effects upon the observed aqueous pressure, although the maximum rate employed gave somewhat lower results, especially when the gas was dried before passing it into the calcium bromide tube.

Morley[1] has shown that phosphorus pentoxide leaves not more than 1 mg. water in 40,000 liters of air. Blank experiments with our apparatus showed a gain in weight of the phosphorus pentoxide tube averaging 0.3 mg., so that the values recorded below represent maxima.

TABLE I.—$CaBr_2$.

Temperature centigrade.	Conditions of experiment.	Time. Hours.	Volume of air under standard conditions. Liters.	Weight of water. Gram.	Volume of water vapor under standard conditions. Cc.	Pressure of water vapor. Mm.
0°	Moist	4	7.1	0.0007	0.9	0.10
	Moist	8	7.1	0.0009	1.1	0.12
	Dry	4	7.3	0.0005	0.6	0.06
	Dry	8	7.0	0.0010	1.2	0.13
	Dry	8	7.2	0.0005	0.6	0.06
					Average,	0.09
25°	Moist	4	7.0	0.0015	1.9	0.20
	Moist	4	7.2	0.0015	1.9	0.20
	Moist	2	7.3	0.0011	1.4	0.14
	Moist	2	7.2	0.0007	0.9	0.10
	Moist	2	7.0	0.0007	0.9	0.10
	Moist	8	7.1	0.0013	1.6	0.17
	Dry	4	6.9	0.0012	1.5	0.16
	Dry	4	7.0	0.0013	1.6	0.17
	Dry	3	7.2	0.0015	1.9	0.21
	Dry	2.5	7.2	0.0005	0.6	0.06
	Dry	2.5	7.0	0.0008	1.0	0.11
	Dry	2	7.0	0.0003	0.4	0.04
	Dry	7	6.9	0.0011	1.4	0.15
	Dry	8	7.0	0.0011	1.4	0.15
					Average, rejecting 2-hour determinations,	0.18
50°	Moist	4	7.1	0.0011	1.4	0.15
	Moist	4	7.1	0.0012	1.5	0.16
	Moist	2	7.1	0.0013	1.6	0.17
	Moist	8	7.1	0.0012	1.5	0.16
	Dry	4	7.2	0.0019	2.4	0.25
	Dry	4	7.1	0.0015	1.9	0.20
	Dry	2	7.1	0.0014	1.7	0.18
	Dry	8	7.1	0.0019	2.4	0.25
					Average,	0.19

[1] *Am. J. Sci.*, 34, 199 (1881); THIS JOURNAL, 26, 1171 (1904).

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A second series of experiments was carried out with zinc bromide, which was prepared by allowing bromine which had been distilled from a bromide to act upon commercial C. P. zinc under water. The solution of the bromide was evaporated and fused in a platinum dish. The experiments with zinc bromide were carried out in the same fashion as in the case of calcium bromide, variations of the same sort being introduced.

TABLE II.—$ZnBr_2$.

Temperature centigrade.	Conditions.	Time. Hours.	Volume of air under standard conditions. Liters.	Weight of water. Gram.	Volume of water vapor under standard conditions. Cc.	Pressure of water. vapor. Mm.
0°	Moist	4	7.2	0.0023	2.9	0.30
	Moist	8	7.4	0.0018	2.2	0.23
	Dry	4	7.1	0.0022	2.7	0.29
	Dry	8	7.2	0.0023	2.9	0.31
					Average,	0.28
25°	Moist	4	7.14	0.0090	11.2	1.23
	Moist	8	7.04	0.0084	10.5	1.12
	Dry	8	6.96	0.0083	10.3	1.12
					Average,	1.16
50°	Moist	8	7.38	0.0484	60.7	6.36
	Moist	8	7.36	0.0476	59.3	6.23
	Dry	8	7.35	0.0357	44.5	4.66*
	Dry	8	7.08	0.0490	61.0	6.42
					Average, rejecting the starred experiment,	6.34

The preceding table indicates that the first hydrate of zinc bromide has an aqueous vapor pressure six times as great as that of calcium bromide at ordinary temperatures, and that the increase in this aqueous vapor pressure with the temperature is very much more rapid than with calcium bromide. Evidently calcium bromide is very much better suited as a drying agent than zinc bromide.

Finally, in order to compare zinc chloride with sulfuric acid and calcium chloride for drying hydrochloric acid gas, similar experiments were made with zinc chloride.

Morley[1] found that sulfuric acid leaves only 0.25 mg. of water in 100 liters of air, while Dibbits[2] found the aqueous vapor pressure of the lowest hydrate of calcium chloride to be 0.29 mm., 2.17 mm., and 3.50 mm. at 0°, 24°, and 30° respectively. Evidently zinc chloride is less well suited for drying hydrochloric acid gas than sulfuric acid, but more so than calcium chloride.

[1] *Am. J. Sci.*, 30, 141 (1885).
[2] *Z. anal. Chem.*, 15, 159 (1876).

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TABLE III.—$ZnCl_2$.

Temperature centigrade.	Conditions.	Time. Hours.	Volume of air under standard conditions. Liters.	Weight of water. Gram.	Volume of water vapor under standard conditions. Cc.	Pressure of water vapor. Mm.
25°	Dry	4	7.1	0.0066	8.2	0.88
	Moist	4	6.9	0.0063	7.8	0.84
	Dry	8	7.0	0.0064	8.0	0.85
	Moist	8	7.0	0.0063	7.8	0.83
					Average,	0.85
50°	Dry	4	7.05	0.0164	20.4	2.16
	Moist	4	6.90	0.0243	30.2	3.25*
	Dry	8	7.05	0.0115	14.3	1.51*
	Moist	8	6.92	0.0167	20.8	2.24
	Moist	8	6.97	0.0163	20.3	2.18
					Average, rejecting starred experiments	2.19

To summarize the results of this research, the aqueous vapor pressures of the lowest hydrates of the three salts examined are found to have the following maximum values:

	0° Mm.	25° Mm.	50° Mm.
$CaBr_2$	0.09	0.18	0.19
$ZnBr_2$	0.28	1.16	6.34
$ZnCl_2$	..	0.85	2.19

The weights of residual water in one liter of a gas dried at 25° by these salts and by calcium chloride and sulfuric acid are:

	Gram.
$CaBr_2$	0.0002
$ZnBr_2$	0.0011
$ZnCl_2$	0.0008
$CaCl_2$	0.0021
H_2SO_4	0.000003

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 184.]

A SIMPLE CONSTANT-TEMPERATURE BATH FOR USE AT TEMPERATURES BOTH ABOVE AND BELOW THAT OF THE ROOM.

BY J. LIVINGSTON R. MORGAN.

Received January 12, 1911.

The apparatus described in this paper is for the purpose of maintaining any desired temperature, from a little above 0° to one in the neighborhood of 90°, with an accuracy of a few hundredths of a degree. The principle of the method of regulating the temperature, in few words, is to deliver to the bath, as it is necessary, water[1] which is either higher or lower in

[1] Foote (*Z. physik. Chem.*, 33, 740 (1900)) has used this principle in a less con-

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temperature, according as the fixed temperature lies above or below that of the room or of an ice or warm-water bath surrounding the lower portion of the bath. The air of the room is thus made, for medium temperatures, to act as a cooler for the higher temperatures, or a heater for the lower ones; but is aided for the extremes of each.

The general plan of the apparatus, for the convenience of those who wish to make up one with the least trouble, is shown in some detail in the figure. The regulator is of the kind which allows the mercury meniscus to attain approximately the same position at all the temperatures—the turning of a stopcock, after the desired temperature is reached, causing the subsequent expansion or contraction of the liquid to affect the meniscus and to maintain that temperature. The usual and most convenient form of this is of a U-shape, one side of which is a tube 3 cm. in diameter and about 15 cm. long, to which is attached a small funnel provided with a stopcock; at the bottom of this tube a platinum wire is fused into the glass. The lower part of the other side of the U is capillary (6 mm. in diameter, the bore being 0.75 mm.). This tube extends upwards for about 6 cm., the continuation being of tubing with a bore of 4 mm. After enough mercury has been added to the bulb side to bring the smaller meniscus, in the capillary, to a point about 3 cm. below the top of the capillary, the rest of the bulb, including the funnel tube, is filled in the usual way with toluene. A threaded collar, fastened with a thumb screw and provided with a binding post, is now attached to the wider continuation of the capillary tube. Through this collar passes a threaded brass rod (2 mm. in diameter), to the lower end of which is soldered a short piece of platinum wire, 0.5 mm. in diameter. By screwing this rod up or down, contact with the meniscus in the capillary can be made at any desired temperature around that at which the stopcock was turned; the stiffer rod, carrying the short piece of platinum wire, allowing greater delicacy of movement than would be possible with a piece of slender wire of the same length, such as would be necessary were the whole tube capillary, instead of being widened at its upper end.

The water, at a higher or lower temperature, which is to be added automatically to the bath is contained in a constant-level vessel, so arranged that the water pressure cannot exceed 40–50 cm. of water. So long as this pressure is not exceeded, the height of the level may vary.

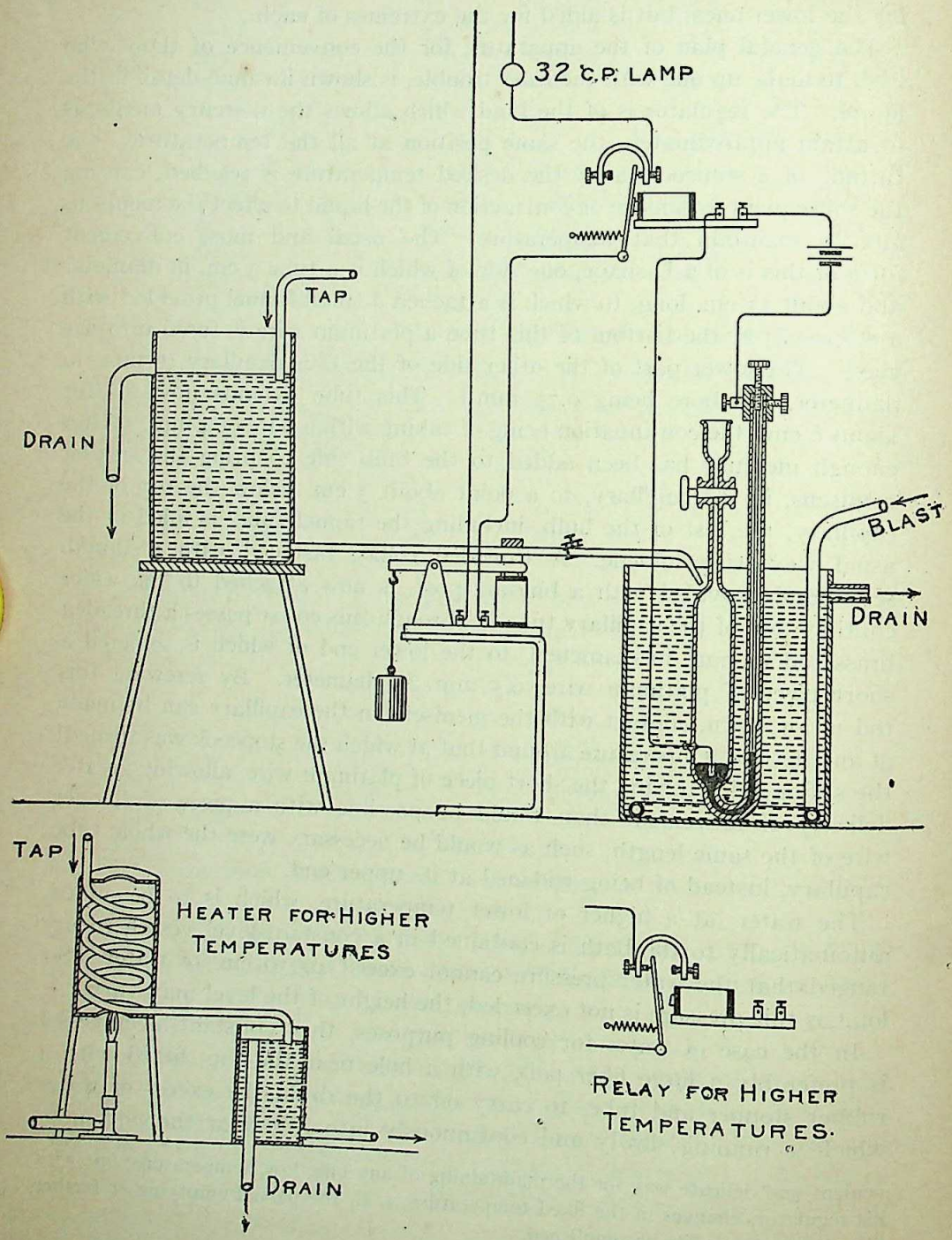
In the case of water for cooling purposes, this constant-level vessel is preferably a large fiber pail, with a hole near the top, fitted with a rubber stopper and tube, to carry off to the drain the excess of water which is running slowly and continuously into it. Near the bottom is

venient and delicate way for the maintaining of any one, low, temperature; but with his regulator, changes in the fixed temperature, *i. e.*, the partial emptying or further filling, are not readily accomplished.

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another, similar, hole, fitted also with a rubber stopper, containing a 5 cm. glass tube. It is through this that the water to supply the bath flows. When lower temperatures are desired, this pail is filled partially with cracked ice or snow; for continuous running in this way, the pail



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of course should be large enough to contain a supply of ice sufficient for twenty-four hours, or should be wrapped with felt, or placed in a refrigerator.

For a warm water supply the constant-level vessel is simply a metal can of about 500 cc. capacity, fitted with an overflow leading to the drain, and an outlet at the bottom. The tap-water which runs slowly and continuously into this is first heated by passage through a copper coil placed over a burner, or through any one of the quick water heaters to be found on the market. The speed of flow of the tap water here regulates approximately the temperature of the supply water, and should be such that that of the constant-level vessel is at least 5° or 10° above that to be maintained in the bath.

For temperatures up to 10° the bath itself would best be placed in another and lower vessel filled with ice, or snow, and salt, which will give the bath a temperature that is too low. The water flowing in in this case is tap water, which *raises* the temperature of the bath as it is necessary.

For temperatures above 50°, it is best to place the bath in a lower vessel, into which the water from the coil flows directly and continuously at a temperature about 5° above that desired. Tap water is run in here by the regulator to *cool* the bath, as that is necessary.

The bath itself may be a battery jar of 2 or 3 liters capacity, or even a large beaker. 3 cm. from its top should be a hole, provided with a rubber stopper, through which runs a glass tube to carry off to the drain the excess of water. Stirring is most simply obtained by blowing air through a single coil of tin pipe placed at the bottom and bored with four small holes. A pump for this purpose can be very simply made from a filter pump and a tin tank with an overflow, if no continuous blast is available.

The two platinum wires of the regulator are connected with the binding posts of a dry cell or a storage cell, in series with a small relay, which must be used to prevent sparking in the regulator. This relay is so arranged that the house circuit, in series with a 16 or 32 candle power lamp, can be either made or broken in a large telegraph sounder connected to the other two terminals of the relay. This sounder has attached to it a bar of brass, about 5 mm. above the lowest position of the arm, when it is attracted by the magnet. The other end of the sounder arm has attached to it by wire a weight of several pounds, so that when no current is passing through the sounder, the arm presses tightly against the brass bar.

The thin rubber tube of 4 mm. bore, connected to the outlet of the constant-level vessel, is now run over the sounder arm and under the bar above it. Water is thus allowed to flow from the supply vessel into the bath when the sounder arm is drawn down by the current; at all other times the rubber tube is pinched tightly together by the weight, and the flow of

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water is prevented.[1] The bath should be placed as close as possible to both the sounder and the supply vessel, to prevent any too excessive radiation. The water flowing into the bath should fall upon the regulator, so that the effect of the change in temperature is most marked at that point. To secure this result the inflow tube is attached directly to the regulator by the clamp holding that in position.

For temperatures requiring that the bath be cooled by the inflowing liquid, the water, either at tap temperature or in contact with ice, is allowed to flow through the rubber tube leading over the sounder to the bath, the stopcock of the regulator being open and the platinum wire in contact with the mercury meniscus, until the bath is filled with water at the desired temperature. The addition of warmer water may also be desirable if time is an object. When the desired temperature is obtained in the bath, the stopcock of the regulator is turned off, and the threaded rod moved sufficiently to raise the platinum wire, which has been in contact with the mercury, to a point just above it, thus breaking the current and shutting off the supply of cold water. The relay in this case must close the circuit in the sounder when the bath becomes too warm, *i. e.*, when the mercury is in contact with the platinum point. So soon as the air of the room, or its aids, causes this to take place, then, the circuit is again closed, in both relay and sounder and the weight is lifted, allowing cold water to flow in until the mercury falls away from the platinum point, when once again the weight drops and shuts off the water. If the volume of water flowing in is too great, it will be noticed that the temperature continues to fall, even after the water is shut off. This can be avoided by regulating the speed of flow in the beginning with a screw pinchcock placed on the rubber tube, between the sounder and the bath. The cock should be so fixed that the effect of the supply water added ceases as soon as it is shut off.

When the bath is to be heated by the flow of supply water, just as before, as soon as the desired temperature is reached the stopcock of the regulator is turned off.[3] Here, however, contrary to the lower temperature case, the supply water must be turned on when the bath is too cool, hence the sounder arm must be drawn down by the current when the mercury and platinum are *not* in contact, *i. e.*, when no current is passing through the relay. In order to bring this about the positions on the relay of the insulated screw and the platinum-pointed one are exchanged, so that the current will flow through the sounder when it is *not* passing

[1] This principle, without the weight, has already been used in a similar way to regulate the flow of gas.

[2] It is well to fix the desired temperature in the bath as exactly as possible (by working the sounder by hand) *before* turning the stopcock, and regulating the platinum wire; for otherwise mercury may be driven beyond the platinum, forming small globules which destroy the regulation.

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through the relay. In the original filling of the bath in this case, then, the mercury and platinum must not be in contact until after the stopcock is closed, when the wire is screwed down so that it just makes contact. As this contact is broken, owing to the cooling of the bath, the relay current is also broken, which causes current to flow through the sounder, drawing down its arm and allowing warmer water to flow in until contact is again made, when the weight carries down the unattracted arm and pinches the rubber tube.

The advantages of this apparatus are as follows:

Any temperature, between 0.1° and 90°, can be maintained, with an accuracy of a few hundredths of a degree, in one form of bath, which is simple, easy to adjust and inexpensive.

A small and transparent bath can be employed without sacrifice of delicacy.

A series of determinations, such as specific gravities, each at a different temperature, can be made in a day, for but a short time is required to change from one constant temperature to another.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY No. 185.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. III. AN APPARATUS FOR RAPID AND ACCURATE DETERMINATION OF THE WEIGHT OF A FALLING DROP OF LIQUID.

BY J. LIVINGSTON R. MORGAN.

Received January 12, 1911.

Introduction.

The results obtained in the previous researches of this series,[1] employing the cumbersome and elaborate apparatus necessary for the calculation of the weight of a falling drop from the very accurately determined volume of a single falling drop of the liquid, and its density, have shown that for all the (6) liquids studied[2] the weight of the drop is strictly proportional to the surface tension of the liquid at that temperature; and can be substituted very satisfactorily for the latter in the relationship of Eötvös, as modified by Ramsay and Shields.

Since, contrary to the conclusions of all the other investigators in this field, the weight of a falling drop of liquid from any one tip is thus found to

[1] Morgan and Stevenson, THIS JOURNAL, 30, 360–76; *Z. physik. Chem.*, 63, 151–70 (1908). Morgan and Higgins, *Ibid.*, 30, 1055–68; *Ibid.*, 64, 170–86 (1908).

[2] Work with the new apparatus on about 50 new liquids, in place of contradicting this, confirms absolutely all the conclusions, with regard to this relationship, reached in the two previous papers.

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be strictly proportional to its surface tension, determined by capillary rise, or any other accurate method; and since from the surface tension of a liquid, and consequently from its drop weight, the molecular weight and some of the physical constants of the liquid can be accurately calculated,[1] it is quite evident that a simple, yet accurate, laboratory apparatus for the determination of the weight of a falling drop of liquid would be of value in the study of the liquid state.

The object of this paper is to present the specifications for such an apparatus, so simple and easy to operate (in contrast to capillary rise and other methods) that it can serve, for general laboratory purposes, in much the same way as the freezing-point and boiling-point methods; and yet, at the same time capable of giving results fully as accurate as those by Morgan and Higgins, *i. e.*, with a mean error of but a few hundredths of 1 per cent.

What at first appeared to be a very simple problem, however, was soon found in reality to be a very complicated one. This discovery, together with the delays in the work of glass blower and grinder, and the definit setting aside of a year and a half for a thorough testing of the method in the hands of several observers, in order to bring to light, if present, any unforeseen errors or defects, is the cause of the somewhat considerable delay in the publication of the description of this simpler form of apparatus. In its final form, as here presented, consequently, all difficulties have been avoided or eliminated, so that at length an apparatus is at hand with which any one can confirm readily (and with even a smaller mean error) the results already presented on the weight of a falling drop, or those to be presented in the future.

In order to duplicate accurately the results of Morgan and Higgins it was at once recognized that the only satisfactory, simple method possible was one based upon the direct determination of the weight of a number of falling drops; for the observation of the number of drops falling from a definit weight of liquid is only fairly accurate, even when the evaporation is reduced to zero; and here it was desired to obtain results of the greatest possible accuracy, at temperatures up to within a few degrees of the boiling point. For such a method it is clear that the following conditions must be fulfilled, if the results of Morgan and Higgins are to be duplicated:

1. Perfect and absolute control of the speed of formation of the drop up to the instant of its fall,[2] and the ability to weigh accurately any number of fallen drops.

[1] In later papers of this series will be considered the relationship existing between molecular weight and the physical constants and the drop weight from any one tip.

[2] It is quite evident, though apparently disregarded by most investigators, that *the weight of a falling drop can only be proportional to its surface tension when the drop*

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2. Avoidance of, or compensation for, any loss of liquid by evaporation from either the hanging drop, or from the drops which have already fallen, at temperatures even up to within a few degrees of the boiling point; this to include also any of the evaporation which is possible owing to the difference of vapor pressure caused by the difference in curvature of the liquid surfaces, *i. e.*, hanging drop and liquid from the fallen drops.

3. Exact knowledge of the temperature (and assurance of its constancy) of the liquid as it forms the drop.

4. Assurance that the tip is always horizontal; or at any rate is always exactly in the same position, if it is not horizontal.

5. Certainty that succeeding drops are always identical; in other words, the avoidance of errors which might be due to consecutive dropping, and consequently not observed when the weight of the first, perfect drop is found, as in the method of Morgan and Higgins.

These conditions, together, naturally, with the possibility of cleaning the apparatus thoroughly, without destroying its setting, were recognized at once as essential features of any accurate method for finding the weight of a falling drop of liquid; and all are very satisfactorily fulfilled in the form of apparatus which is here advocated.

It is unnecessary here to show how the above difficulties were met one by one, and avoided; to sketch the various other forms which were found for one reason or another to be inadequate and discarded; or to consider the almost numberless other difficulties which were encountered; so that we can proceed at once to the description of the apparatus, and the method of carrying out a determination with it.

The Apparatus.

The essential parts of the apparatus are shown in section in Fig. 1. Since it is more satisfactory for the worker to set up the apparatus for himself, rather than to allow the maker to attempt it, the details are entered into more fully here than would otherwise be necessary. Be-

is caused to fall by its own weight alone, and is not blown out from the tube by an excess of pressure applied to it through the tube. In other words, when the weight of the hanging drop *just exceeds* the surface tension of the liquid, which maintains the drop form, it ruptures and falls. And yet many investigators state that to avoid evaporation losses they have caused the drops to fall rather rapidly; which violates the above premise, and, in general, causes more liquid to fall than otherwise would.

Since it is only at the instant of fall that this condition must in general be fulfilled, the drop can be formed very rapidly, and checked just before it is allowed to fall, so that it is only the weight of the drop itself which causes the rupture; or the drop can be formed very slowly throughout its entire life, as was the case in the work of Morgan and Higgins, where the viscosity of the liquid in the very long capillary buret absolutely and automatically prevented anything but a very slow and uniform speed of formation.

This question is considered again later.

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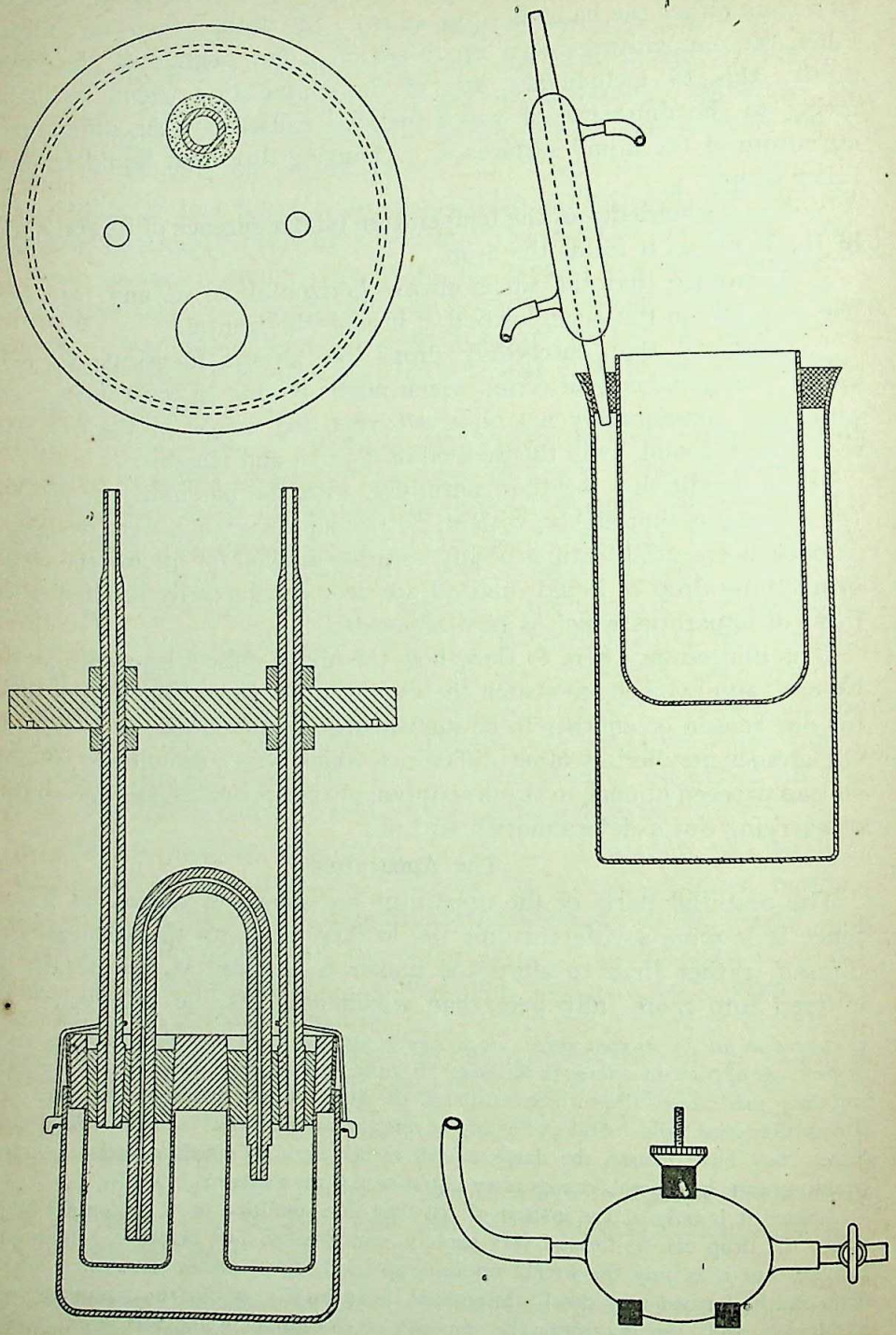


Fig. 1.

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fore being cemented together the apparatus consists of the following separate pieces:[1]

One glass disk (7 × 1.5 cm.), in which there are three holes; one of these, 1 cm. in diameter, is 5 mm. from the edge of the plate, lying on one diameter; the other two are side by side, on the other diameter, with their edges separated by 7 mm., and are slightly smaller at the bottom than at the top, where the diameter is 2.2 cm. There are four hooks of wire cemented into holes in the lower side of this plate, one each on opposit sides of the two large holes.

Two plugs which are so ground into the two holes of the disk that their tops lie 6 mm. below the top of the plate, while at the bottom they project 8 mm. below the plate. In each of these plugs there are two 6.5 mm. holes.

Two light weighing vessels (3.5 cm. deep), which are provided with light ground-in glass stoppers. These are also ground to fit tightly on the lower projections of the plugs (when the latter are in position), where they are held by rubber bands fastened to the wire hooks on the plate.

One capillary dropping tube (6 mm. in diameter, with a bore of 0.2 mm.[2]) which is bent in Π-shape, one end being 9 mm. in length, while the other, the tip side, is 7.0, the separation of the legs being such that if one leg is put through the inner hole of the one plug, the other falls into the adjacent hole of the other plug, when these are in position in the disk. The tip side is ground down, concentric to the bore, to the diameter desired for the tip, for a distance of 0.5–1 cm. The tip itself has a straight, sharp edge, as is shown in the figure, and must be handled with the greatest of care.[3]

Two ventilation tubes, 15 cm. long and 6 mm. in diameter, with a bore of 2–3 mm. At the upper end these are drawn out to one-half the diameter, while the lower ends are ground into the outer hole of the plugs, so as to extend 1–2 mm. below them.

One air vessel, 4 cm. high and large enough to fit loosely on the glass disk. A pair of glass hooks are attached on opposit sides of this vessel, near the top.

[1] The apparatus in this form can be obtained from Messrs. Eimer and Amend, of New York City. Without the very skillful work of their grinder, much of the work on drop weight done in this laboratory would have been utterly impossible, and I wish here to acknowledge my indebtedness to his skill.

[2] The bore here should be such that liquid even in very small amounts forms a thread, and consequently can be removed completely from the bore by suction or pressure.

[3] Such straight-edged tips could not be obtained at the time of the work of either Morgan and Stevenson or Morgan and Higgins, but the grinder has since discovered that by first beveling the edge, and then just grinding it off, sharp edges, free from chips and flaws, can readily be obtained.

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One air tube, 14 cm. long and 1 cm. in diameter, the lower end of which is ground into the third hole of the glass disk. The top of this hole should be larger than the bottom, *i. e.*, it should be funnel-shaped at the top, so that amalgam may be packed around the tube, after it is in position, to protect the cement from the effects of water. The object of this air tube is to prevent a vacuum being formed in the air vessel when the apparatus cools, after being removed from a warm bath.

One glass cover disk to hold together the above parts. This is 1 cm. thick and 10.5 cm. in diameter, with a 9.5 cm. groove, 3 mm. deep, parallel to the edge. In this disk there are two pairs of holes, one pair on each diameter. Two of these holes are 8 mm., the other two, 2.2 cm. in diameter.

One stiff rubber compression bulb, provided at one end with a tube carrying a stopcock, and attached at the other to a meter of rubber compression tubing, 5 mm. in diameter, with a bore of 1 mm. This is so arranged in an Ostwald clamp that it may be compressed or expanded with great delicacy by the turning of the milled screw head.

One reading glass (8–10 cm. in diameter), on a stand, by the aid of which the formation of the drop may be followed.

It is well to have duplicates made of the tip tube, the weighing vessels, and the air vessel, so that in case of an accident no time will be lost.

To assemble the apparatus, the plugs are first cemented into the holes in the disk with "stratina" or any other glass cement, care being taken that they are in such a position that the tip tube will slide through the adjacent holes; and the ventilation tubes, when pushed into the outer ones, will also enter the corresponding (8 mm.) holes in the cover disk. After the plugs are cemented into the disk, and the ventilation tubes into the plugs, all is allowed to stand until the cement has hardened. The two vessels, the weighing vessel on the tip side, and the supply vessel on the other, are now fitted perfectly air-tight to the projecting ends of the plugs, using lanolin, since in the setting up suction is to be applied for a long period and the rubber tube from the bulb connected to the tip ventilation tube, while the top of the other ventilation tube is plugged by a piece of rubber tubing containing a glass rod. All is now in readiness for the fastening in of the tip tube. In order to do this most conveniently, the disk is set upon two parallel pieces of wood fastened together at the ends with two blocks, so that the plate can rest solidly upon the pieces of wood, while the vessels slip between them.

The tip tube is to be so arranged that the shoulder formed by the grinding down to form the tip reaches at least to the bottom of the plug, or extends slightly below it. It can be held temporarily in this position by allowing the supply end to rest upon a piece of folded paper, of the proper thickness, placed in the bottom of the supply vessel. A piece of asbestos cord is now shredded out and the finer pieces packed around

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the tip tube, on both sides, with a small chisel-shaped awl, until it is firmly held in the proper position. The holes here should be about 0.5 mm. larger than the diameter of the tip tube, so that the lengths of asbestos can be packed around both legs uniformly. This is really more satisfactory than attempting to have the legs ground into the holes, for that is not only difficult to accomplish, but, if once accomplished, makes the tip tube too rigid to stand the changes in temperature necessary, and causes it in time to crack at the bend. After the joints have been packed with asbestos, "stratina" is placed on the upper layer and suction applied with the rubber bulb. Any leak in the joints is now made apparent. In case there be such, the cement is allowed to harden, still applying suction, and more asbestos and "stratina" supplied until the apparatus is tight enough to stand, without change, the full suction of the bulb over night. It is probable, here, that when properly set up the "stratina" does not penetrate the lower layers of the asbestos, for the use of such an apparatus for a year, using volatil liquids, even within a few degrees of their boiling point, has never shown any trace of substance dissolved by the vapors. In case difficulty is experienced in this respect, however, the tip side may be raised so that the shoulder is just within the plug, when a ring of lead, cut from a sheet, may be packed in, which will prevent any such action, except for the vapors of corrosive liquids.

The air tube is now fastened into the third hole of the disk with "stratina," the dry cement both here and on the plugs being covered with a layer of plaster of Paris moistened with linseed oil (or a mixture of barium sulfate, graphite, and linseed oil) and then packed tightly with an amalgam made by dissolving tin foil to saturation in mercury at 70°. Or the amalgam alone can be used for this purpose. These protect the cement from the action of water; and yet can be readily removed with a knife blade, in case of accident, so that the apparatus can again be taken apart by simply soaking in hot water.

Next, after removing the rubber tubes, the upper extremities of the air and ventilation tubes are passed through the holes in the cover disk, which is to be fastened 10–11 cm. above the other one, the air tube being fastened by a rubber stopper in one of the large holes, while each ventilation tube is cemented to two tightly fitting blocks of wood or glass, which lie one above, and the other below the plate, to which they are to be cemented. It is more convenient to secure the tubes in this way, indirectly to the top, than to have them fit directly and tightly into the cover, for then the holes would have to be smaller in diameter than they are, and there would be danger, if they were not separated by exactly the correct distance, of breaking the tubes in putting on the cover.

A piece of rubber tubing such as is used for Gooch crucibles is now slipped over the edge of the lower disk, overlapping both above and below,

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and is built up with other pieces, if necessary, until the air vessel fits water-tight on the lower few millimeters—thus leaving enough of the upper edge of the disk exposed to furnish a grip for one hand when taking off the air vessel, after a determination, and so to remove any danger of shearing off the ventilation tubes with the twisting strain. Or short pieces of a heavy glass rod may be cemented into two holes, on opposit sides of the upper surface of the disk, for this purpose; but the former plan has been found to be quite satisfactory, especially if the disk be a few millimeters larger at the top than at the bottom, *i. e.*, is cork-shaped.

The next and final step in the setting up is to find what position of the cover is necessary to cause the bottom of the tip to be horizontal, so that it may always be placed in that position for every determination. This may be readily done when putting on the cover disk by being assured that this is parallel to the bottom of the tip, before cementing it fast. Then it will be only necessary to see that the cover is level in two directions before each determination. To do this most readily, a microscope cover glass is temporarily fastened on the bottom of the tip with a drop of glycerol, and the cover moved until observation of the edges of the two surfaces, from all directions, shows it to be parallel to the tip, when it is cemented. If this has not been done in the setting up, it is necessary to find with a level mounted on three legs (two of which are adjustable) the unlevelness of the cover which is necessary to make the bottom of the tip horizontal. Before each determination, then, the adjusted level, fixed previously in the proper position, must be placed on the three marks on the cover, and this raised or lowered until the bubble is fixed on its mark.[1]

The Temperature Bath.

In order to find the temperature of the drop which is forming and falling, it is necessary that the apparatus be immersed in water below the bend of the tip tube. The temperature of the tip tube itself, or the exposed parts must, naturally, be the temperature of the liquid as it drops, for in going slowly through this mass of glass, the small amount of liquid must quickly get into equilibrium with it, even though the temperature of the supply liquid be slightly different. Heating in an air bath, which would allow the use of a much simpler form of dropping apparatus, is not feasible, although much time was expended in discovering it. For this reason, it may be concluded that this form of apparatus, devised for use in a water bath, is the simplest possible, if the temperature is to be fixed exactly.

[1] In the nine pieces of apparatus which are in constant use in this laboratory, this has been necessary, owing to the fact that the ventilation tubes were ground into the cover, thus allowing only one position for that, which was usually not the correct one. These levels were made especially by W. and L. E. Gurley, of Troy, N. Y.

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The water bath, which must, of course, be transparent, would best be the one for all temperatures, from 0–90°, very recently described by Morgan.[1] In this the apparatus itself would be set upon a brass ring (2–3 cm. deep) which just fits into the groove in the cover plate, and is fastened permanently into the cover of the water bath, which would have to be fixed so that it could be raised and lowered, in order to reproduce the unlevelness of the top which is requisit to level the tip. This can be done by the use of small pieces of wood or card, or the bath itself can be placed upon a stand fitted with three leveling screws.

If such a bath is not at hand, the one shown in the figure may be used, which is heated by the vapor of a boiling liquid. The water vessel here is 18 cm. high and 9.5 cm. in diameter, its top fitting into the groove of the cover disk; or the top may be placed upon a brass ring which is held in place in a larger water vessel with a cork. The outer vessel is a 2.5 liter Jena beaker, the bottom of which is covered with a layer of glass beads to facilitate the bubbling. The cork ring of the outer vessel is provided with a condenser, and is wrapped tightly with tinfoil to prevent the vapor from condensing in it and splitting the beaker. By pouring a layer of plaster of Paris over this tinfoil-covered cork ring, after the water vessel is in place, and coating this with a layer of the tin amalgam, the loss of vapor is reduced to a minimum, and solutions, as well as pure liquids, can be used as the boiling liquid. On any one day, using ether or chloroform, for example, the temperature of the water bath can be retained constant to within a tenth of a degree. From day to day, however, the temperature obtained will naturally change with changes in the barometric pressure. The first heat for ether and the second for chloroform, on the usual small electric stove give very satisfactory results. Just as in the above water bath, the tip here is leveled by aid of pieces of wood or card, or the stove is placed upon an adjustable stand.

Making a Determination of the Weight of a Falling Drop.

Before using the apparatus, the dropping tube and the ventilation tubes should be thoroughly cleansed with bichromate-sulfuric acid, water, alcohol, and ether (especial care being taken that all traces of lanolin are removed) and dried in a current of air. The weighing vessel, *i. e.*, the one on the tip side, is now cleaned and wiped dry with a piece of cheesecloth and placed in position on its plug, and a rubber band, which is attached to one hook, passed over its end and hooked around the other. The tube from the bulb is now connected to the tip ventilation tube, and pressure applied to the bulb, with its stopcock closed, by turning the screw head of the clamp. Sucking the drop over in this way allows a regulation which is utterly impossible when blowing it over, and further, the escape of vapor is thus blocked by the liquid on the one side and the bulb on the

[1] See the preceding paper.

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other. Still retaining pressure on the bulb, the supply vessel, one-half full of the liquid to be investigated, is next put upon its plug, and fastened by a rubber band, as the other was. The purpose of the air pressure here is to prevent the liquid rising in the bore of the capillary to any distance above the surface of the supply liquid, until the determination is about to be made, when the liquid will flow through the *dry* bore, and thus cannot, by any possibility, drive before it small threads of liquid, such as might form, and remain unobserved, if the liquid at first filled the bore, and was then driven back. The air vessel is now put tightly in position on the disk, to protect the two vessels from the water of the bath, and fastened on each side by a rubber band running from the hook, around the lower part of the ventilation tube, and then around the hook again.

The apparatus is then put into the constant-temperature bath and allowed to stand until it has attained the proper temperature, *i. e.*, from 20–40 minutes. It should never be allowed to remain any longer than necessary in the water, and especially not over night, for, if it is, a leak is likely to develop, which will necessitate at least a new packing with amalgam, if not a new setting of the tip. The thermometer bulb should always be just at the bend of the tip tube, and midway between the two legs; it is held by a cork in the second large hole of the cover. A small thermometer placed in the air tube, with its bulb within the air vessel, sometimes shows a difference of 0.2°, but the correct temperature of the liquid, as it drops, as mentioned above, is that of the tube through which it passed, *i. e.*, that of the outside thermometer. While standing in the bath, the top is brought, by use of a level, to the position necessary to assure the constant, horizontal, position of the bottom of the tip. During this period of waiting, pressure must still be applied to the bulb, to keep the meniscus in the lower part of the supply end of the tip tube. Naturally, if the temperature is higher than that of the room, this object will be attained automatically, for the air in the weighing vessel warms more rapidly than the liquid, and having no other outlet, forces that back in the bore.

The temperature now being fixed, the bottom of the tip in its proper position, and the bulb one-half compressed; the liquid is sucked over very slowly, by releasing the pressure screw, until it forms a drop on the tip. It is here that the perfect and absolute control of the drop is apparent, when viewed through the reading glass; especially if the apparatus is placed against a light background, when the bright spot of light in the drop shows increases and decreases that could not be observed in any other way. It is well at this time to practice controlling the drop (*i. e.*, not attempting to make a weighing at first), as it will save much time and trouble later. When a weighing is to be made, the drop, once formed on the tip, is allowed to hang there, being kept at as near its maximum

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size as possible, for 5 minutes. This is for the purpose of saturating the weighing vessel with vapor, so as to free the first drop which is to fall from changes due to evaporation, which might make its speed control difficult. At high temperatures, *i. e.*, near the boiling point, the amount of liquid necessary to saturate the weighing vessel with vapor is at times equal to the weight of one falling drop.

After the drop has hung for 5 minutes, 30 consecutive drops are allowed to fall, the count being kept on a tally register. *It must be borne in mind here that each drop at the instant of its fall must be forming with infinitesimal speed, and hence finally fall of its own weight alone.* The bright spot in the drop, seen through the reading glass against an illuminated white background, must be followed very closely during the formation, and the greatest care exerted, especially at the very last instant, to see that the above condition is fulfilled. The speed of formation, except at this final moment, may be comparatively rapid, so that the fall of the 30 drops will not necessarily require more than 15–30 minutes. Perhaps the best method of taking the drop is to start with such a suction on the bulb that the drop forms rather rapidly, and then gradually and continuously to decrease it until the bright spot shows only the slightest possible increase in size, and the drop falls of its own weight alone. When the last drop has fallen, the remaining portion on the tip is forced back very slowly until the meniscus is just at the tip end of the bore, the bore itself remaining full. When the liquid is anywhere near its boiling point, and perhaps it is best in all cases, the total time which has elapsed from the bringing over of the evaporating drop to the instant when the meniscus is fixed in the tip, is taken.

The apparatus is now removed from the bath and placed with the cover resting on a rubber-covered ring (an opening which allows the apparatus to be slipped in quickly), roughly dried with a towel, and the air vessel taken off. All this should be done as rapidly as possible. Next the supply vessel is removed, care being taken that the liquid in the capillary remains with its meniscus at the tip, which should be watched closely throughout. Then the supply end of the tip tube is touched with a piece of cheesecloth (if necessary the bulb being slightly compressed) until the liquid in the bore is drawn, as a column, and not broken up into threads, into the cloth, without the loss of any of the vapor which takes its place. When assured that there is no trace of liquid left in the capillary bore, a small glass containing water at room temperature (or iced for very volatil liquids) is raised around the weighing vessel so that the water rises a little higher than the liquid within it; it is retained in in this position for 1 minute. This causes the condensation of the vapor in the vessel, tip tube and ventilation tube, and also removes to the main amount any of that which may already have condensed

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on the plug or on the tip—and in addition cools the liquid itself, so that the loss by evaporation during the removal of the vessel from its plug and the immediate insertion of the glass stopper is reduced to a minimum. This transfer should always be made as rapidly as possible, notwithstanding, and in the same way each time.

In weighing the vessel which contains the liquid that has fallen, the most satisfactory method is to wipe it to constant weight with a piece of cheesecloth, *i. e.*, after the first, approximate weight has been obtained, the vessel and stopper are wiped again and again, until further wiping does not change the weight, observed immediately after the wiping. The glass stopper of the vessel must naturally fit tightly, else losses on the balance will be observed, in case the liquid is volatil; while for very volatil liquids (boiling within 5–15° of room temperature) a cork must be substituted for the glass stopper, and a preliminary test made to show that no loss is observable after the vessel, which has stood for 10 minutes on the balance, is wiped and weighed.

The weight observed here, it must be remembered, is not, of course, the weight of the vessel plus that of the 30 drops, for it is increased by the weight of the vapor formed from the hanging drop in 5 minutes, and decreased by that of the vapor lost, both from the hanging drop and from those that have fallen, which may not have been condensed by the cold water. We cannot then simply subtract the weight of the empty vessel, plus that of the vapor formed from the hanging drop in 5 minutes, and expect to have the weight of 30 drops, except when the temperature is such that there is practically no evaporation, *i. e.*, when the vapor pressure at that temperature amounts to but a few millimeters. Furthermore, there may have been a distillation from the hanging drop to the liquid of those which have fallen, or *vice versa*—this would not be accounted for.

In order to take into account all these possible complications, and to eliminate them, the weighing vessel is cleaned and wiped dry and then replaced in position, after the tip ventilation tube and the tip tube have been cleaned with ether and dried with a current of air; and the apparatus set up again, exactly as before, and placed in the bath at the same temperature. Then, once again, when the temperature equilibrium is established and the cover leveled, a drop is run over and allowed to hang for 5 minutes; and then 5 consecutive drops are caused to form and fall, exactly as they did in the case of the 30. Here, however, the liquid is not immediately run back, but the 6th drop is allowed to hang at its maximum size (nearly), until the same total time has elapsed (from the running over of the evaporating drop to the fall of the last one) as in the case of the 30, when it is drawn back until the meniscus is just at the tip. The

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apparatus is now removed, everything being done exactly as it was before, and the weighing vessel and stopper wiped to constant weight.

This weight, of course, will not be the weight of the vessel and 5 drops alone, but is the weight of these plus the vapor of 1 drop hanging for 5 minutes, *minus exactly the same total weight lost by evaporation, from every source, in the 30-drop determination.* By subtracting the weight of this 5-drop *blank* from the weight of the 30 previously determined, we must have the weight of 25 drops of the liquid falling from the tip in question, from which we can find the weight of a single falling drop, unaffected by evaporation, even though the temperature lies within a few degrees of the boiling point. Naturally, if the evaporation from the fallen drops is so great that the 5 drops no longer cover the bottom of the vessel, and present the same evaporating surface as the 30 did, 10 drops may be used as the blank, in which case the subtraction would give the weight of 20 in place of that of 25.

Whether or not all the possibilities of loss have been considered here, it is not possible to decide; it is quite certain, however, that this method of using a blank gives consistent results at all temperatures, even to within 4° of the boiling point.

In using this method it is very necessary with a new liquid to be assured that perfect control is possible at the very last instant before the fall of the drop, for otherwise a false result will be obtained. The question of the control of the drop usually resolves itself into a question of the size of the tip, and its relation to the size of the drop formed upon it. Thus the volume of a drop of carbon tetrachloride is so small that it is impossible to control it readily on a tip larger than 4.6 mm., for it suddenly spurts at the last instant and leads to results that are too large. This can always be predicted, however, from observation of the first drop. Thus far in the work no liquid has been found which can not be controlled easily on a tip of this size, while all liquids, with one or two exceptions, can be controlled easily on tips up to 6 mm. or larger.

Another necessary precaution is to see that the second and succeeding drops are identical in size, *i. e.*, that consecutive drops lead to the same result as a single drop. It is sometimes observed with pyridine that the second drop is smaller than the first. The remedy for this, and it should always be used at least once with a new liquid, is after the first drop has fallen to run the remainder back until the meniscus is just at the tip, and to start the second drop from there, and to continue in this way until the desired number of drops have been obtained. This difference is usually to be observed through the glass as a change in the profile of the drop. It is possible that this result is due to the fact that the remaining drop as it settles back into place after the fall assumes a different form from that which it would assume if it formed from the bore by

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slowly collecting. Whatever the cause, however, the method advocated eliminates it; while in all other cases this method gives the same result as the regular one.

In the next paper of this series will be considered the standardization of a tip, and the calculation, from the drop weight, of surface tension and the molecular weight; while in the succeeding ones, which will appear in the immediate future, will be presented the results already obtained with the fifty or more liquids examined, using tips of various diameters.

LABORATORY OF PHYSICAL CHEMISTRY.

SOLUBILITY OF OXYGEN IN SEA WATER.

BY GEORGE C. WHIPPLE AND MELVILLE C. WHIPPLE.

Received December 19, 1910.

It is a well recognized fact that oxygen is less soluble in sea water than in fresh water, and that in brackish water the solubility is intermediate, varying with the amount of chlorine present. In studying the pollution of the waters of harbors it is often desirable to express the amount of oxygen present in terms of "per cent. of saturation." Inasmuch as the proportion of sea water varies considerably in different samples it is not easy to determin this percentage on account of the lack of convenient tables showing the amount of oxygen dissolved in saturated waters containing different amounts of chlorine. For this reason the authors have investigated the literature on the subject and have prepared a convenient table for use.

One of the earliest investigations of the solubility of oxygen in sea water was made by Prof. William Ditmar, of Anderson's College, Glasgow, in connection with the Challenger expedition.[1] His method consisted of boiling off the dissolved gases, collecting and analyzing them. His results have been much used. They show the variations in the amount of oxygen in "sea water" dissolved at different temperatures, but do not state fully the corresponding amounts of chlorine in the water used for the experiments.

In connection with the study of the amount of dissolved oxygen in the Thames River, Clowes and Houston carried on some experiments on the solubility of oxygen in distilled water, sea water, and mixtures of the two in different proportions, at temperatures between 13.8° and 16° C.[2] The data thus secured, taken in connection with the known variations

[1] "Report on Composition of Sea Water," by William Dittmar, *Challenger Report, Physics and Chemistry*, 1, 168. See also page 58 of the Report of Letts and Adeney on the "Pollution of Estuaries and Tidal Waters," Appendix 6 of the "Report of the Royal Commission on Sewage Disposal, 1908."

[2] Report to the London County Council by Dr. F. Clowes and Dr. A. C. Houston on "The Experimental Bacterial Treatment of London Sewage, 1892-1903," page 225.

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in the amount of oxygen dissolved in distilled water at different temperatures, have been used as the basis of determining the per cent. of saturation in brackish waters.

Believing that the importance of the subject demanded further investigation, the authors undertook some careful experiments to determin the solubility of dissolved oxygen in sea water of known chlorine content at temperatures of 0°, 10°, 20°, and 30°. Winkler's method was used. Saturation was obtained by forcing a current of air through three liters of water in a bottle so jacketed that a constant temperature was obtained. Determinations were made at intervals and continued until a constant result was reached. This sometimes took several hours.

While these experiments were in progress we received, through the courtesy of Dr. Howard T. Barnes, of McGill University, a paper by Dr. Charles J. J. Fox, on "The Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea Water and of Atmospheric Carbonic Acid in Sea Water,"[1] which covered the ground so completely that it seemed unnecessary for us to continue our work, especially as the results obtained by Fox agreed with our own, as far as they had been carried.

Fox's results were obtained by exposing the water to an atmosphere of pure dry oxygen and measuring the quantity of gas dissolved. For the practical use of water analysts it is necessary to transform the data thus obtained into the units commonly used, namely, milligrams per liter, or parts per million. Fox himself has given a table in which the results are expressed in terms of cubic centimeters of oxygen absorbed per liter from a dry free atmosphere containing 20.9 per cent. of oxygen at 760 mm. pressure, as follows:

NUMBER OF CC. OF OXYGEN ABSORBED BY 1000 CC. OF SEA WATER FROM A FREE DRY ATMOSPHERE CONTAINING 20.9 PER CENT. OF OXYGEN OF 760 MM. PRESSURE.

$$1{,}000a = 10.291 - 0.2809t + 0.006009t^2 + 0.0000632t^3 - \mathrm{Cl}\,(0.1161 - 0.003922t + 0.00006311t^2).$$

Chlorine, parts per million.	$t = 0°$.	4°.	8°.	12°.	16°.	20°.	24°.	28°.
0	10.29	9.26	8.40	7.68	7.08	6.57	6.14	5.75
4,000	9.83	8.85	8.04	7.36	6.80	6.33	5.91	5.53
8,000	9.36	8.45	7.68	7.04	6.52	6.07	5.67	5.31
12,000	8.90	8.04	7.33	6.74	6.24	5.82	5.44	5.08
16,000	8.43	7.64	6.97	6.43	5.96	5.56	5.20	4.86
20,000	7.97	7.23	6.62	6.11	5.69	5.31	4.95	4.62

For convenient use we have corrected these figures for vapor pressure and have transformed them into parts per million. These results are herewith presented with the hope that they may be of service to sanitary engineers and water analysts.

[1] *Trans. Faraday Soc.*, Sept., 1909, p. 68.

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DISSOLVED OXYGEN IN DISTILLED WATER AND IN SEA-WATER OF DIFFERENT DEGREES
ATMOSPHERE CONTAINING

(Calculated by G. C. Whipple and M. C.

Temperature centigrade.	Distilled water.[1]	Chlorine in Sea-Water (parts per million). 0.	1000.	2000.	3000.	4000.	5000.	6000.	7000.	8000.	9000.
0	14.70	14.62	14.45	14.29	14.12	13.96	13.79	13.63	13.46	13.30	13.13
1	14.28	14.23	14.06	13.90	13.73	13.57	13.41	13.25	13.09	12.93	12.77
2	13.88	13.84	13.68	13.52	13.36	13.20	13.05	12.90	12.74	12.59	12.43
3	13.50	13.48	13.32	13.17	13.02	12.87	12.72	12.58	12.43	12.28	12.13
4	13.14	13.13	12.99	12.84	12.70	12.55	12.41	12.26	12.12	11.98	11.84
5	12.80	12.80	12.65	12.51	12.37	12.23	12.09	11.95	11.81	11.67	11.53
6	12.47	12.48	12.34	12.20	12.06	11.93	11.79	11.66	11.52	11.39	11.25
7	12.16	12.17	12.03	11.90	11.77	11.64	11.51	11.37	11.24	11.11	10.98
8	11.86	11.87	11.74	11.62	11.49	11.37	11.24	11.12	10.99	10.86	10.73
9	11.58	11.59	11.46	11.34	11.22	11.09	10.97	10.85	10.73	10.60	10.48
10	11.31	11.33	11.20	11.08	10.97	10.85	10.73	10.60	10.48	10.37	10.25
11	11.05	11.08	10.96	10.84	10.73	10.61	10.49	10.38	10.26	10.15	10.03
12	10.80	10.83	10.72	10.61	10.50	10.39	10.28	10.17	10.06	9.94	9.83
13	10.57	10.60	10.49	10.38	10.27	10.16	10.05	9.95	9.84	9.73	9.63
14	10.35	10.37	10.27	10.16	10.06	9.95	9.85	9.74	9.63	9.53	9.42
15	10.14	10.15	10.05	9.95	9.85	9.75	9.65	9.55	9.45	9.35	9.25
16	9.94	9.95	9.85	9.75	9.65	9.56	9.46	9.36	9.26	9.16	9.06
17	9.75	9.74	9.64	9.55	9.45	9.36	9.26	9.16	9.07	8.97	8.88
18	9.56	9.54	9.44	9.35	9.25	9.16	9.07	8.99	8.90	8.80	8.71
19	9.37	9.35	9.26	9.17	9.08	8.99	8.89	8.80	8.71	8.63	8.54
20	9.19	9.17	9.08	9.00	8.91	8.82	8.73	8.65	8.56	8.47	8.38
21	9.01	8.99	8.91	8.83	8.74	8.65	8.57	8.48	8.40	8.31	8.23
22	8.84	8.83	8.75	8.67	8.59	8.50	8.42	8.33	8.25	8.16	8.08
23	8.67	8.68	8.60	8.52	8.44	8.35	8.27	8.18	8.10	8.02	7.93
24	8.51	8.53	8.45	8.37	8.29	8.20	8.12	8.04	7.96	7.87	7.79
25	8.35	8.38	8.29	8.21	8.12	8.04	7.96	7.88	7.80	7.72	7.64
26	8.19	8.22	8.14	8.06	7.98	7.90	7.81	7.73	7.65	7.57	7.50
27	8.03	8.07	7.99	7.91	7.83	7.75	7.67	7.60	7.52	7.44	7.36
28	7.86	7.92	7.84	7.76	7.68	7.61	7.53	7.45	7.37	7.30	7.22
29	7.74	7.77	7.69	7.62	7.54	7.47	7.39	7.31	7.23	7.15	7.07
30	7.60	7.63	7.55	7.48	7.40	7.33	7.25	7.17	7.09	7.01	6.93

[1] The figures in this column are those of the Committee on Standard Methods

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OF SALINITY WHEN SATURATED AT DIFFERENT TEMPERATURES AND EXPOSED TO AN 20.9 PER CENT. OXYGEN.

Whipple from measurements of C. J. J. Fox.)

10000.	11000.	12000.	13000.	14000.	15000.	16000.	17000.	18000.	19000.	20000.	Difference per 100 parts per million of chlorine.
12.97	12.80	12.64	12.47	12.31	12.14	11.98	11.81	11.65	11.48	11.32	0.0165
12.61	12.46	12.30	12.14	11.98	11.82	11.67	11.51	11.35	11.19	11.03	0.0160
12.28	12.13	11.98	11.83	11.67	11.52	11.37	11.22	11.06	10.91	10.76	0.0154
11.98	11.83	11.68	11.54	11.39	11.24	11.09	10.95	10.80	10.65	10.50	0.0149
11.69	11.55	11.40	11.26	11.11	10.97	10.83	10.69	10.54	10.40	10.25	0.0144
11.39	11.26	11.12	10.98	10.84	10.70	10.57	10.43	10.29	10.15	10.01	0.0140
11.12	10.99	10.85	10.72	10.58	10.45	10.32	10.18	10.05	9.91	9.78	0.0135
10.85	10.73	10.60	10.47	10.34	10.21	10.09	9.96	9.83	9.70	9.57	0.0130
10.61	10.48	10.36	10.23	10.11	9.98	9.86	9.73	9.61	9.48	9.36	0.0125
10.36	10.24	10.12	10.00	9.88	9.76	9.64	9.52	9.40	9.28	9.17	0.0121
10.13	10.02	9.90	9.78	9.66	9.55	9.44	9.33	9.21	9.09	8.98	0.0118
9.92	9.81	9.69	9.58	9.46	9.35	9.24	9.13	9.02	8.91	8.80	0.0114
9.72	9.61	9.50	9.39	9.28	9.17	9.06	8.95	8.84	8.73	8.62	0.0110
9.52	9.41	9.30	9.19	9.09	8.98	8.87	8.76	8.66	8.56	8.46	0.0107
9.32	9.22	9.11	9.01	8.90	8.80	8.70	8.60	8.50	8.40	8.30	0.0104
9.14	9.03	8.93	8.83	8.73	8.63	8.53	8.43	8.33	8.23	8.14	0.0100
8.96	8.86	8.77	8.67	8.57	8.47	8.38	8.28	8.18	8.08	7.99	0.0096
8.78	8.68	8.59	8.49	8.40	8.30	8.20	8.11	8.02	7.93	7.84	0.0095
8.62	8.52	8.43	8.33	8.24	8.15	8.07	7.98	7.88	7.79	7.70	0.0092
8.45	8.36	8.27	8.18	8.09	8.00	7.91	7.82	7.74	7.65	7.56	0.0089
8.30	8.21	8.12	8.03	7.95	7.86	7.77	7.68	7.60	7.51	7.42	0.0086
8.14	8.05	7.97	7.88	7.80	7.71	7.62	7.54	7.45	7.37	7.28	0.0086
7.99	7.91	7.83	7.74	7.66	7.57	7.48	7.40	7.31	7.23	7.14	0.0085
7.85	7.76	7.68	7.60	7.51	7.43	7.34	7.25	7.17	7.08	7.00	0.0083
7.71	7.63	7.54	7.46	7.38	7.30	7.21	7.13	7.05	6.96	6.87	0.0083
7.56	7.48	7.40	7.31	7.23	7.15	7.07	6.99	6.90	6.82	6.74	0.0082
7.42	7.34	7.26	7.18	7.10	7.02	6.94	6.86	6.78	6.70	6.61	0.0080
7.28	7.20	7.12	7.04	6.96	6.88	6.81	6.73	6.65	6.57	6.49	0.0079
7.14	7.06	6.99	6.91	6.83	6.75	6.68	6.60	6.52	6.44	6.37	0.0078
7.00	6.92	6.83	6.77	6.70	6.62	6.55	6.47	6.40	6.32	6.25	0.0076
6.86	6.79	6.72	6.64	6.56	6.49	6.43	6.35	6.28	6.20	6.13	0.0075

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of Water Analysis of the American Public Health Association.

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A STUDY ON THE PHENOLSULFONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

[THIRD PAPER.]

THE CHIEF SOURCES OF ERROR IN THE METHOD.

By E. M. Chamot, D. S. Pratt and H. W. Redfield.

Received December 19, 1910.

Soon after the method, known also as the Grandval and Lajoux or Sprengel method, became known and quite generally adopted by water analysts, perplexing variations in results and peculiarities in the behavior of the reagents used were reported by many; but it is only within comparatively recent years that a thorough systematic study of the method has been made, the earlier work being abortive because of incomplete knowledge of the composition of the reagent and of the composition of the colored reaction product upon which the entire method depends. The evolution and improvement of the method has already been summarized in the two preceding papers[1] and need not here be again discussed.

For the purposes of study and discussion the chief errors which may affect the results as obtained by the method as now in use may be conveniently grouped under the following heads:

I. Errors resulting from
  a. The use at different times of sulfonic acids of varying composition.
  b. The use of reagents of different ages and therefore of changing composition.
II. Errors resulting from the use at different times of varying volumes of reagent.
III. Errors resulting from variable time of contact between reagent and water residue.
IV. Errors due to differences in the temperature of the water residue and standard when the reagent is applied or those resulting from a great rise in temperature when the alkali is added.
V. Errors due to variations in the alkali employed.
VI. Errors due to the presence of organic matter.
VII. Errors due to losses through evaporation.
VIII. Errors due to the presence of carbonates.
IX. Errors due to the presence of chlorides in the residue.
X. Errors due to the presence of iron.
XI. Errors due to the presence of other forms of interfering inorganic compounds not covered above.

The attention of water analysts has been called to most of these sources of error by many previous investigators, nevertheless, it has been thought best to again review all these difficulties and it is the purpose of this paper to discuss in a brief manner these sources of errors and point out the shortcomings of the phenolsulfonic acid method as now practiced and to suggest what appears to be a marked improvement in the process whereby it is possible to eliminate the worst of the troubles.

[1] Chamot and Pratt, This Journal, 31, 922; 32, 630.

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For convenience the sources of error above listed will be taken up for discussion in the order given.

I. a, b. Errors Due to the Variable Composition of the Reagent.—The fact that the composition and method of preparing the sulfonic acid reagent affected the delicacy of the method and influenced the intensity and shade of the yellow color of the reaction products appears to have been early recognized by analysts, since the literature of this method contains many directions for making reagents in greatly varying proportions of phenol and sulfuric acid and in the subsequent treatment of the mixture.

These reagents fall into four broad classes.

A. Those made by mixing phenol and concentrated sulfuric acid at ordinary temperatures.[1]

B. Those made by mixing phenol and concentrated sulfuric acid to which a little water has been added.[2]

C. Those made by mixing phenol and concentrated sulfuric acid and adding thereto a little concentrated hydrochloric acid.[3]

D. Those made by heating a mixture of phenol and concentrated sulfuric acid.[4]

Until the compound giving the yellow color in the alkaline solution had been isolated and purified, great difficulty was experienced in studying the errors of the method, as no satisfactory and reliable standards could be prepared which would not themselves be subject to part of these same sources of error. The color top, color wheel and tintometer suggested themselves but proved impracticable. As soon, however, as the pure tripotassium nitrophenoldisulfonate was obtained, a means of preparing standards of exactness and permanence became available. It was now possible to weigh out portions of this compound containing known amounts of nitrogen and prepare a series of standards whose color was found to remain unchanged for many months. Moreover, these standards could be diluted with computed volumes of water and still show the correct color tint and intensity in a colorimeter corresponding to the reduced nitric nitrogen content.

The importance of the discovery of this method for the preparation of invariable standards made from the actual color compound will be appreciated by all readers. Directions for preparing tripotassium nitrophenoldisulfonate will be found given in our fourth paper. In order that the results of colorimeter reading should be as free as possible from

[1] Lombard, *Bull. soc. chim.*, [4] 5, 1092 (1909).

[2] Smith, *Analyst*, 10, 199 (1885); Girard and Lajoux, *Compt. rend.*, 101, 62 (1865); Rideal, *Chem. News*, 60, 261 (1889).

[3] Johnson, *Chem. News*, 61, 15 (1890); Farcy, *Bull. soc. chim.*, [4] 5, 1088 (1909).

[4] Gill, *Tech. Quart.*, 7, 55 (1894); THIS JOURNAL, 16, 122 (1894).

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the personal equation, in all the work described below, the colors were read in turn by two and usually three observers, absolutely independently and with the key to the strengths of solutions or methods being investigated in the hands of one observer only. It was thus possible to eliminate bias and preformed opinions.

The reagents falling under Class A may vary greatly in composition, depending upon the proportions of phenol and sulfuric acid, upon the way in which the materials are mixed and upon the age of the reagent. In sulfonic acid reagents of this type it is possible to have the orthosulfonic acid remain in the mixture only when no great excess of sulfuric acid is used; otherwise the mixture as first made contains a little ortho, much para and some disulfonic acids. Moreover the amount of the disulfonic acid increases with the age of the reagent. These facts we have been able to prove by analyses of practically all the types of reagents by the methods already described by us in papers I and II. By way of illustration the most recently described reagent, that of Lombard,[1] is made by mixing phenol and concentrated sulfuric acid at room temperature. When freshly prepared this was found to contain large amounts of mono acids. Nitrate-containing water residues treated with this fresh reagent and made alkaline in the usual manner showed in the colorimeter greenish tints, as was to be expected, instead of pure yellows. After ten days the sulfonation had progressed so that nearly all the acid was now phenol-disulfonic acid. Greenish colors in the final product were now obtained only when the residue and reagent were warm. After standing six months little further change could be detected.

It is evident that these variations in the composition of reagents of Class A must introduce decided errors where results of analyses made at one time are to be compared with those obtained at another time, inasmuch as there is both a variation in the final products of the reaction and a variation in the sensitiveness of the reagent. This is especially true if permanent standards are employed. Reagents of Class A type must be allowed to stand some time before use. Since, however, the rate of sulfonation is indefinit and not easily measured, there is no certainty when an equilibrium has been reached. Moreover, it has been shown[2] that the orthosulfonic acid gives greens in the final product in the cold, the intensity of the green being proportional to the amount of ortho acid present, thus giving rise to great variations in the colorimeter readings and rendering comparisons with results obtained with different reagents impossible.

The parasulfonic acid, on the other hand, gives final green colors only when warmed in contact with the nitrate. But it must be remembered

[1] *Bull. soc. chim.*, [4] 5, 1092 (1909).

[2] Paper I, *loc. cit.*

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that in this contact, unless special precautions are taken, sufficient heat is generated to nitrify the para acid; moreover, when water is added to dilute the reagent after contact a marked rise in temperature again results, which is further increased when the alkali is added to develop the color. When much para acid is present, green tints must thus invariably result unless the water residue is kept in a freezing mixture during the addition of reagent, water and alkali. The greater the rise in temperature the more intense is the greenish tint. Thus here too a decided error is introduced.

Reagents falling in Class B and Class C have the same faults as those of Class A. It follows, therefore, that any sulfonic acid reagent of greatly varying composition must be regarded as undesirable and that the more stable the reagent is and the smaller the number of component sulfonic acids the better and more reliable will be the results obtained.

Since the final yellow product whose color intensity is measured, in arriving at the amount of nitric nitrogen present in a sample of water, is due to an alkali salt of nitrophenoldisulfonic acid,[1] it follows that reagents of Class D are best and most reliable. This was long ago shown by Gill.[2] Heating the phenol with the concentrated acid accomplishes, in a short time, a degree of sulfonation which only very long standing could bring about.

Gill's reagent having been found to be the best of those proposed and having been adopted by the American Public Health Association, it has been termed the "standard" reagent in the preceding papers and has been selected in the present instance for the study of the sources of error given above. In his paper describing his method for the preparation of the disulfonic acid reagent Gill stated no reasons why the ratio of 3 grams of phenol to 37 grams of sulfuric acid was adopted. It was therefore first necessary to ascertain the proper proportion of phenol and sulfuric acid in reagents which could be prepared by the heating method. With this end in view mixtures were made varying in composition from 1 gram molecule of phenol with 1–16 gram molecules of sulfuric acid. All were heated for six hours at 100° in the usual manner. It was found that the best and clearest yellow colors were obtained when the mixture contained 12 or more gram molecules of sulfuric acid. This proportion is that of Gill's reagent and fully confirms his work. Moreover, it was further found that reagents containing less sulfuric acid would solidify after standing several days in a cool place, owing to crystallization of the sulfonic acid.

The Gill or standard reagent, however, still contains sufficient mono-para acid to yield greenish tints if the reagent is poured upon a warm

[1] Chamot and Pratt, THIS JOURNAL, 32, 630.

[2] *Tech. Quart.*, 7, 55 (1894); THIS JOURNAL, 16, 122, 193 (1894).

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nitrate-containing residue, or if there is a marked rise in temperature either upon dilution with water or upon the addition of alkali, thus introducing marked errors at times and of very different degrees. The standard reagent is therefore not a safe or satisfactory one, particularly if permanent standards are employed. The conversion of all of the phenol into the disulfonic acid by the method described later, with the elimination of the small quantity of mono acid still present in the standard reagent, removes at once these sources of difficulty.

II. Errors Due to Variable Volumes of Reagent.—It has been quite generally assumed that providing a volume of the sulfonic acid reagent sufficient to cover the water residue is used it makes little difference whether this volume be much or little within certain narrow limits, although Leffmann[1] appears to have recognized the importance of using exactly equivalent volumes on the known and unknown nitrate residue. This assumption that the color is independent of the volume of reagent used is not warranted, however, the facts being that the final color is actually greatly influenced by the volume of the reagent employed, the intensity increasing with the volume and when more than 4 or 5 cc. of the standard reagent are used, greenish colors appear in the final alkaline liquid. Murky tints almost impossible to match in a colorimeter are also often produced even when no green is discernible. With volumes of reagent in excess of 5 cc. a large amount of inorganic sulfate usually separates, occluding sufficient of the yellow compound to necessitate dilution beyond the capacity of the colorimeter cylinders commonly employed.

The following table shows the average apparent increase of nitrate due to increasing volumes of standard reagent used, the lowest volume being here assumed for purposes of comparison as the correct value.

Cubic centimeters of standand reagent used.	Water residue with N indicated in parts per million.				
	2 parts.	4 parts.	6 parts.	8 parts.	10 parts.
1 cc. taken as.....	2	4	6	8	10
2 cc. equivalent to.....	2.3	4.4	6.6	8.8	11.1
3 cc. equivalent to.....	2.7	5.1	7.7	10.0[3]	13.1
4 cc. equivalent to.....	3.2	5.6[2]	8.2	11.0[3]	14.2[3]
5 cc. equivalent to.....	4	6.4[2]	9.8[2]	12.9[4]	15.5[4]

These results clearly show that there is a very decided error unless the standard reagent is very carefully measured and exactly the same volume is employed in treating both the known nitrate-containing residue and that of the sample of water being examined. Practically identical re-

[1] "Examination of Water," page 52.
[2] Murky tints difficult to compare with the 1 cc. color.
[3] Greenish tint.
[4] Very green.

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sults as to intensity are obtained when the reagent contains no mono acids, except that in this case neither murky nor green tints develop.

The commonly accepted procedure has been to employ 2 cc. of sulfonic acid. This volume gives satisfactory colors, of sufficient intensity and free from murky or greenish tints and there is therefore no good reason to depart from this volume now used by common consent, but it must be borne in mind that this volume must be carefully measured, if accurate results are required.

Thinking that the very marked increase in color resulting when large volumes of reagent are used might possibly be due in part to ionic concentration and to variation in dissociation, runs were made using a variety of radical combinations, *e. g.*, sodium, potassium, ammonium, magnesium, and calcium nitrates as sources of nitric nitrogen. The concentration of the sulfate ions was also varied by the addition of potassium sulfate. In all cases the final colors were the same both in tint and intensity.

Since the green tints and colors are due to nitrification of monosulfonic acids and since it had already been ascertained that the standard reagent gave green tints only when warmed with nitrates, it appeared probable that the darker colors and changes in tint observed with volumes of reagent greater than 2 cc. resulted from the rise of temperature that naturally followed when stronger acid was neutralized. This heat, curiously enough, seems to account for the changes in color intensity shown in the table.

The color obtained by using 4 cc. of standard reagent is almost exactly matched if to 2 cc. of reagent, 2 cc. of concentrated sulfuric acid is added. Moreover, if 2 cc. of reagent be used, water added and the whole kept boiling while the alkali is added, it is found that the resulting yellow color is darker than that obtained in the usual manner; *e. g.*, with residues containing 10 parts of nitrogen as nitrate per million the following results were obtained:

2 cc. of reagent taken as = 10 parts N.
2 cc. of reagent + 2 cc. of H_2SO_4 = 13.4 parts N.
2 cc. of reagent neutralized hot = 11.3 parts N.

If the elevation of temperature causes the apparent increase in the nitrate content, the reverse should hold true. This has been confirmed experimentally by treating the cold residue with the standard reagent, diluting with cold water and keeping at 0° by means of cracked ice while the cooled alkali was slowly added. It was found that in all cases the final colors obtained were of less intensity than when the usual practice was followed, the apparent difference being less by 0.2–0.4 of a part per million according to the volumes of reagent used. This discrepancy is here again due to the presence of mono acids, since with reagents containing only the disulfonic acid, equivalent volumes of re-

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agent give identical final color intensities irrespective of whether cooled with ice or not.

III. Errors Resulting from Variable Time of Contact between Reagent and Residue being Treated.—In a reaction involving the introduction of nitro groups into a sulfonic acid an appreciable length of time is necessary in order that the final product shall show the full content of nitrogen. In order that the minimum time might be ascertained a number of experiments were performed, all of which showed that the reagent and residue should remain in contact at least two minutes after the complete covering of the residue. By way of illustration it is necessary to cite only one of the series of trials made. In this, residues containing 10 parts per million of nitrogen as nitrate were compared with the pure tripotassium nitrophenoldisulfonate standards.

Time of contact.	Parts N found.
15 seconds	8.8
30 seconds	8.9
1 minute	9.2
2 minutes	10
5 minutes	10
10 minutes	10
19 hours	10

In obtaining contact between reagent and all particles of residue the best practice is to mix the two with a glass rod, crushing all particles that may be found. With waters high in total solids containing little nitrate it is essential that the particles be crushed and that a contact of over two minutes be allowed.

IV. Errors Due to Differences in the Temperature of the Residue when the Reagent is Applied.—Richards and Hollings[1] have pointed out that the final color varied greatly with the temperature at which the reagent acted upon the residue. The usual procedure in America has been to allow the residues obtained by evaporation on the water bath to cool to room temperature before applying the reagent. It has already been shown in the present paper that the final color is greatly intensified by temperature. With reagents containing monosulfonic acids all sorts of variations in intensity and tint are obtained if the reagent be applied to a hot residue and very serious errors result if standard nitrate and water residue are not treated exactly alike as to temperature. Failure to observe this precaution leads to enormous errors. Should the reagent be applied at once to the residue upon its removal from the water bath so much green appears in the final product as to render impossible a comparison with a nitrate standard prepared at room temperature. The greater the proportion of monosulfonic acids present the greater will be the deviation from the yellow color of the nitrate standard.

[1] *Soc. Chem. Ind.*, 22, 616 (1903).

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If a reagent consisting wholly of disulfonic acid be employed, there is no change whatsoever in color intensity caused by heating and no green tints appear. It has been possible to heat reagents of this type for over three hours on the water bath in contact with nitrate residues and still obtain the same brilliant yellow as that of the permanent nitrate standard.

V. Errors Due to Variations in the Alkali Employed.—It has long been recognized that the same alkali must be added to the water residue being tested as that with which the standard has been prepared. But there do not appear in the literature any data showing just what the difference in color intensities may be when using different alkalies nor which alkali gives the darkest color and therefore permits of the recognition of the smallest amount of nitric nitrogen.

In the method as originally described, ammonium hydroxide was employed to render the liquid alkaline and develop the yellow color. Ammonia fumes are decidedly objectionable in a laboratory devoted to water analyses where determinations of free and albuminoid ammonia must be made. Where such conditions obtain a fixed alkali must be substituted in accordance with the suggestion of Hazen and Clark[1] but these investigators give no data upon which to base a decision as to the alkali to be preferred. It was also important that experiments be performed in order to learn the influence if any that an excess of alkali might have on the color.

It had already been ascertained that potassium hydroxide gave yellow colors as intense or slightly more so than the other alkalies,[2] hence the employment of the tripotassium salt of the nitrophenolsulfonic acid as standard.

Experiments were made to ascertain the effect of variable excess of alkali. The following table shows the average results obtained by using varying volumes of 12 normal alkali in excess. In these runs the residues contained 6 parts and 10 parts per million of nitrogen as nitrate respectively.

Comparisons were made with the permanent tripotassium salt standards.

PARTS PER MILLION NITROGEN INDICATED.

Cubic centimeters 12 *N* alkali in excess.	With KOH.		With NaOH.		With NH_4OH.	
	6 parts.	10 parts.	6 parts.	10 parts.	6 parts.	10 parts.
Just alkaline.....	6	10.2	5.2	9.2	4.1	7.5
2 cc.....	6	10	5.2	8.9	4.8	8.5
5 cc.....	6	10	5.3	9.0	4.9	8.8
10 cc.....	6	10	5.6	9.2	4.9	9.5
Over 10 cc.....	.	10	...	9.2	...	9.5

[1] *J. Anal. Appl. Chem.*, 5, 301 (1891).

[2] Chamot and Pratt, *loc. cit.*

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Other trials with different nitrate content were made with relatively similar results. It appears therefore that potassium hydroxide yields darker colors and that a decided excess of alkali does not appreciably affect the results. In the case of potassium hydroxide, however, it is essential that there be always an excess, since the color just at the neutralization point is slightly reddish and therefore appears darker than when there is a drop or two in excess. For reasons not ascertained ammonium hydroxide has yielded variable results, but since this alkali was otherwise undesirable no further investigations were made.

VI. Error Due to the Presence of Organic Matter in Water.—The residue from a water containing organic matter, when acted upon by the strong sulfuric acid of the reagent, gives rise to brown colors, either before or after the alkali is added, that often completely mask any yellow due to nitrates. This source of error has been so long known and so well recognized that comparatively little time was spent in its study. Many methods have been suggested for removing the organic matter, such as potassium permanganate in acid solution, or in alkaline solution, basic lead acetate, animal charcoal, aluminum cream, etc. Of these methods aluminum cream has proved the most satisfactory and practicable in our hands, when dealing with the usual type of waters used for household and municipal purposes in our section of the United States. In all but very exceptional waters the removal of the coloring matter by this process has been found sufficiently complete and no losses of nitrates have been observed.

VII. Errors Due to Mechanical Losses on Evaporation or during the Addition of the Acid Reagents.—Leeds[1] has stated that nitrates are slightly volatil at 100° and Fox[2] has found nitrates in the distillate from a solution of potassium nitrate. Gill[3] found a slight difference in his results ascribed to loss on evaporation but so small as to be considered within the limits of error of the method.

Until the tripotassium salt standard was adopted in the present investigation it was found practically impossible to properly interpret the results obtained, but with an available standard at hand it was found that the losses on evaporation were negligible, and that the slight variations in colorimeter readings of three different observers were as great as any indicated differences which might be ascribed to evaporation losses.

The method employed in this study consisted in evaporating on the water bath equal volumes of water containing known amounts of nitrogen as nitrate. These residues were treated with standard reagent as usual,

[1] *Am. J. Sci.*, [3] 7, 197 (1874).
[2] *Tech. Quart.*, 1, 54 (1887).
[3] *Loc. cit.*

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after various periods of continued heating of the dry residue, and finally were compared with tripotassium nitrophenoldisulfonate standard.

The following are some of the results obtained with 1, 2 and 10 parts per million of nitrogen as nitrate.

Time of heating after residue became dry.	Parts per million of nitrogen found.		
0	1.0	2.0	10.0
30 min.	1.1	1.9	10.0
1 hour	1.0	1.9	10.1
2 hours	1.0	2.0	10.0
4 hours	1.0	2.0	10.2
7 hours	...	...	10.0

The slight differences in the readings are undoubtedly due to the presence of the mono-para acid in the reagent, for runs made with a disulfonic acid reagent free from mono acids gave even better results. Other runs with different quantities of nitrogen were made with similar results. It appeared, therefore, that any losses arising from heating the dry residue in a water bath are not measurable in colorimeters of the types commonly employed. However, it seemed wise to carry the study a trifle farther. After a sample had reached dryness, distilled water free from nitrates was added and evaporated to dryness. This process was continued many times. Finally the residue was treated with the reagent, diluted and made alkaline. No measurable loss of nitrogen could be detected.

The fact that the final colors obtained matched those of the permanent tripotassium salt shows that the thin film of reagent covering the residue is sufficient to hold the nitric acid set free by the strong sulfuric acid of the reagent, and that any losses due to incomplete nitrification are not measurable. Nevertheless, to make assurance doubly sure, samples of water were evaporated in deep crucibles, adding a little at a time so as to have the residue substantially all on the bottom. A rapid application of reagent then gave a much greater thickness of sulfonic acid over the residue. Identical results were thus obtained; in no case was the final color appreciably darker as measured in long Nessler tubes or in a Wolff colorimeter.

The addition of the reagent causes losses in particular cases, however, as for example when carbonates or chlorides are present.

VIII. Errors Due to the Presence of Carbonates in the Water Residue.—The addition of the sulfonic acid reagent to residues containing much carbonate causes more or less violent effervescence due to the liberation of carbon dioxide and a consequent mechanical loss of nitrate, causing in some cases considerable error. This was proved by evaporating waters in round-bottomed flasks, which were then closed with a two-holed stopper carrying a separatory funnel and bent glass tube leading into nitrate-free distilled water. The reagent was added to the residues

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through the funnel and the evolved gases swept over into the distilled water by nitrate-free air; this water was then made slightly alkaline and evaporated to dryness. The residue treated in the usual manner showed the presence of nitrates, while blank tests made on carbonates showed none. No uniform loss was found among many samples of waters having similar nitrate and carbonate contents. This was to be expected, as the exact rate of adding the reagent, and the method and the rapidity of its distribution over the residue would naturally materially effect this loss. This loss, however, is insignificant save when the alkalinity of the water is very high or the amount of nitrate present is very low; when these conditions obtain the loss may be easily prevented by adding to the sample before evaporation an amount of 0.02 *N* sulfuric acid sufficient to nearly but not quite neutralize the alkalinity.

At this stage of the investigation word reached us from Professor Bartow, of the University of Illinois, that he believed that Robert Spurr Weston was at work upon errors due to carbonates. Correspondence with Mr. Weston brought out the fact that he and his assistant, Miss Helen R. Hosmer, had already made sufficient progress on the investigation to demonstrate that carbonates do introduce very appreciable error in the sulfonic acid method.

Weston and Hosmer very kindly placed the results of their investigations in our hand, and it is with great appreciation of their courtesy and kindly interest in our study of the sulfonic acid method that the following results are quoted from their unpublished notes.

"The work was done in March, 1909. We were at a loss to explain the freakishness of the results we were getting with some highly nitrated sewage effluents, and thinking that possibly it might be due to the presence of carbonates, we made a rough experiment as follows:

"Six samples of distilled water, each containing 0.006 mg. of nitrogen in the form of potassium nitrate, were evaporated to dryness, three of them with the equivalent of 2, and three with the equivalent of 5 mg. of calcium carbonate. When treated with phenolsulfonic acid and compared in the ordinary way the approximate readings were as follows:

Milligrams nitrogen taken	Milligrams calcium carbonate, equivalent to sodium carbonate added.	Milligrams nitrogen determined.
0.006	2.0	0.004
0.006	2.0	0.004
0.006	2.0	0.005
0.006	5.0	0.002
0.006	5.0	0.002
0.006	5.0	0.002

"This experiment shows plainly that the presence of carbonates interfered with the formation of color. In order to approximate more nearly

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the conditions found in natural waters the experiment was repeated with smaller quantities, as shown in the following table:

Milligrams nitrogen taken.	Milligrams of calcium carbonate added.	Milligrams nitrogen determined		
		A.	B.	C.
0.005	0.00	0.004	0.004	0
0.005	0.05	0.004	0.004	...
0.005	0.1	0.003	0.004	...
0.005	0.25	0.003	0.003	0.004
0.005	0.5	0.002	0.002	0.003
0.01	0.05	0.008	0.008	...
0.01	0.1	0.007	0.007	...
0.01	0.25	0.006	0.006	0.006
0.01	0.5	0.005	0.005	0.005
0.01	0.00	0.010	0.010	...

"It was evident from this experiment that the carbonate prevented the formation of the yellow color to some extent. To confirm our impressions that this was due to the presence of carbon dioxide, evolved when the acid was added to the residue, and not to the presence of the base (potassium, sodium, calcium, etc.), we evaporated samples containing 0.01 mg. of nitrogen in the form of potassium nitrate to dryness, treated them with phenolsulfonic acid, and after diluting them with water, passed carbon dioxide into three of the samples for about 5, 10 and 25 minutes respectively. The results were as follows:

Milligrams nitrogen taken.	Minutes exposure to CO_2.	Milligrams nitrogen determined.
0.01	5	0.008
0.01	10	0.006
0.01	25	0.005

"These experiments proved that the introduction of the gas destroys the color-producing compound.

"Experiments were made to show whether or not the presence of atmospheric carbon dioxide had any effect upon the determination and for this purpose several samples were evaporated in an atmosphere of dioxide without affecting the determination of the nitrogen. Free carbon dioxide has no effect as it is expelled during evaporation, that is, before the phenolsulfonic acid is added.

"The above were only preliminary experiments and are mainly of suggestive value. They were not continued after we heard that you were studying the determination.

"Our suggestion for the overcoming of this difficulty is to add acetic acid to the water before evaporation. No experiments were made along these lines, however, beyond evaporating some of the standard with such amounts of sodium acetate as would be formed were acetic acid so added. This did not prevent the determining of the full amount of nitrogen present.

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"Whether or not an excess of acetic acid added to ordinary waters would cause volatilization of nitrogen from the acid solution during the evaporation of the samples, we cannot say. We feel sure from our experiments that if the alkalinity of the water be not destroyed by so doing, that it may be used with good results."

In view of the above quoted results, it did not appear necessary to spend further time upon the study of the effect of carbonates on the standard reagent, and all further work was confined to reagents containing no monosulfonic acids. In the latter case, the same small mechanical losses were again observed. No appreciable change in final color could be observed even after 12 hours' passing of carbon dioxide through the treated residue, before the addition of the alkali.

IX. Errors Due to the Presence of Chlorides in the Residue.—When a water contains a large amount of chlorine as chlorides, the nitric nitrogen determined by the phenolsulfonic acid method is much too low. This error has been long recognized, but it is not until very recently that it has been shown that even small amounts of chlorides may cause a most serious error. As long ago as 1891 Bartram[1] called attention to the fact that the age of the reagent had an important bearing upon the magnitude of this error; with a freshly prepared reagent there was little apparent loss, but the same reagent after it had aged furnished results lower than before. This variation in behavior we now know to be due to the gradual change of mono acids into the disulfonic acid.

The low results obtained when a water residue contains chlorides are partially due to mechanical loss and in part due to interaction of the hydrochloric and nitric acids liberated. This was proved by proceeding in the manner already described under the losses due to carbonates. While the investigation was in progress, Farcy[2] arrived at similar results by substantially similar methods. Lombard and Laport[3] had already advanced a similar hypothesis without experimental data. Farcy has also shown[4] that bromides and iodides introduce a similar error. Determinations were made by this author and by Perrier and Farcy of the losses in nitric nitrogen when more than six parts per million of chlorine as chloride were present. The data published show a striking regularity in the proportion of loss to halogen present. The proportional increase in loss with the increase in halogen is such that a correction for error would be possible. But Stewart and Greaves[5] obtained no such proportional regularities. We had already arrived at a similar result. The loss in nitrogen increases with the amount of chlorides present but the

[1] *J. Frank. Inst.*, 131, 385 (1891).
[2] *Bull. soc. chim.*, [4] 5, 1091 (1909).
[3] *Ibid.*, [4] 5, 321 (1909).
[4] *Ibid.*, [4] 5, 178, 563 (1909).
[5] THIS JOURNAL, 32, 756 (1910).

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per cent. of loss is so very irregular that it was not possible to adopt any numerical correction. The more mono acid the reagent contained the greater the variation in the nature of the loss. Even when a reagent containing no mono acids is employed the amount of loss is too irregular with below 10 parts per million of chlorine to permit of correction, but with over 10 parts of chlorine the loss approximates 30 per cent. of the nitric nitrogen. Space forbids the incorporation here of more than one series of experiments by way of illustration. In the table given each water residue contained 10 parts per million of nitrogen as nitrate and the amount of chlorine as chloride indicated. In each case the limits given are from the results of at least five different water residues and in several instances many more. Comparisons were made with a pure tripotassium nitrophenolsulfonate standard.

Parts per million of chlorine present.	Parts per million of N found.	
	Minimum.	Maximum.
0	10	10
0.5	9.35	9.75
1	9.25	9.85
2	8.50	8.75
3	8.30	8.75
4	7.80	8.45
5	7.65	7.80
10	7.20	7.45
15	7.20	7.30
20	7.05	7.35

It appears therefore that the method of procedure for the prevention of error, consisting in the addition of a like quantity of chlorides to the standard as has been determined in the sample, is not always safe and is applicable only when over 10 parts per million of chlorine are present.

When accurate results are required, the halogens must be removed by means of silver sulfate.

Silver compounds have long been employed for the removal of chlorine and prevention of loss. Shaking the sample with silver sulfate is at the present time the method in general use. Shaking with silver oxide has also been suggested,[1] but neither process is satisfactory. Marcille[2] advocates using an ammoniacal solution of known strength, evaporating to dryness, adding the sulfonic acid, diluting as usual and adding ammonium hydroxide to develop the color and dissolve the silver chloride formed. This method has given in our hands perfectly satisfactory results, but is objectionable in a water analysis laboratory because of the ammonia fumes evolved. The procedure which has given us the best results and eliminates ammonia consists in determining the chlorine present in the sample, then adding to the volume of the sample to be

[1] Tatlock and Thompson, *Chem. Ind.*, 23, 428 (1904).

[2] *Ann. chim. anal.*, 14, 303 (1909).

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used for the determination of nitrates such a volume of a solution of silver sulfate as will remove all but about 0.5 of a part per million of chlorine, heating to boiling, adding a little "aluminum cream" to aid in clarifying and to remove color, filtering and evaporating to dryness on the water bath, the residue is then treated with sulfonic acid as usual. As thus practiced the method becomes very little longer than without the removal of chlorides and requires substantially no more time than that of Marcille.

X. Errors Due to the Presence of Iron.[1]—When dealing with ferruginous waters very high in iron a residue is obtained which is penetrated only with great difficulty by the sulfonic acid reagent. The results obtained therefore show great variations. These variations are not however in proportion to the iron present. With the standard or Gill reagent the losses in nitrogen are sometimes very great, but it was found that when the reagent is of such composition as to permit heating in contact with the residue for a few minutes no such discrepancies can be detected. Should the composition of the reagent preclude heating with the residue, the iron must be removed.

The effect of the presence of iron was tried on many samples of water, containing up to 5 parts per million of Fe.

When much iron is present and the alkali used for the development of the color is added very slowly a red or brown solution is obtained whose color is destroyed by the addition of a slight excess of alkali with the formation of a precipitate of iron hydroxide and the usual yellow color of the nitrophenoldisulfonate. The red coloration may thus serve as an indication of the presence of much iron and as a warning that losses of nitrogen may be expected unless the contact of reagent and residue has been unusually intimate.

XI. Errors Due to Other Interfering Inorganic Substances.—Both nitrites and magnesium compounds have been stated at various times to introduce errors of sufficient magnitude to necessitate special treatment of the water.

To test the influence of nitrites, nitrate-free silver nitrite was prepared, decomposed by pure sodium chloride and the resulting sodium nitrite employed.

A large number of water residues containing known added amounts of pure sodium nitrite but no nitrates were treated with the sulfonic acid reagent as usual. It was found that nitrites in amount less than 0.2 parts per million of nitrogen gave no yellow color and therefore had no influence upon the determination, but if present in excess of this value

[1] Drown and Hazen, "Purification of Water and Sewage," Special Report, Massachusetts State Board of Health, 1870, 712.

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the amount of nitric nitrogen is found too high, apparently due to a higher oxidation of part of the nitrogen in the nitrite.

According to Pouget[1] this oxidation takes place in accordance with the equation

$$3HNO_2 = 2NO + HNO_3 + H_2O$$

and is quantitative for amounts of nitrite from 0.1 to 0.3 mg. In the case of nitrites present in water residues, however, we have obtained yields of nitric nitrogen always much below that indicated by this equation, and it is not until the nitrogen reached 1 part per million that the final yellow color was of sufficient intensity to appreciably affect colorimeter readings.

Waters very high in magnesium compounds yield residues whose particles, as in the case of iron compounds, are penetrated only with great difficulty by the sulfonic acid reagent, and it appears that the difficulty lies in failure to obtain intimate contact between reagent and nitrate. Very thorough rubbing with a glass rod is essential. The chief error when dealing with waters high in magnesium chloride is due to the effect of the chlorine and not of the base.

Summary.

1. Sulfonic acid reagents containing mono acids are subject to change with age and yield results greatly affected by temperature, concentration, variation in character of alkali, etc. They cannot be satisfactorily employed with permanent standards.

2. In order that accurate results may be obtained chlorides, carbonates, and organic matter must be removed.

3. Nitrites present in small amount do not appreciably effect the final results, but when exceptionally high must be destroyed or corrected for.

4. A sulfonic acid reagent of definit composition should be used. Such a reagent is described in our fourth paper.

LABORATORY OF SANITARY CHEMISTRY,
CORNELL UNIVERSITY.

A STUDY OF THE PHENOLSULFONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

[FOURTH PAPER.]

A MODIFIED PHENOLSULFONIC ACID METHOD.

BY E. M. CHAMOT, D. S. PRATT AND H. W. REDFIELD.

Received December 19, 1910.

In order that reliable results may be obtained and comparisons with permanent standards shall be possible we have shown that the phenolsulfonic acid reagent must contain no monosulfonic acid.[2]

[1] *Bull. soc. chim.*, 7, 449 (1910).

[2] THIS JOURNAL, 32, 1630 and preceding paper.

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After studying many methods of preparation the following is suggested for trial by water analysts.

Preparation of Phenoldisulfonic Acid Reagent.—Dissolve 25 grams of pure white phenol in 150 cc. of pure concentrated sulfuric acid, add 75 cc. of fuming sulfuric acid (13 per cent. SO_3), stir well, and heat for two hours at about 100°.

The reagent thus prepared contains no mono acids, and no tri acids so far as we have been able to ascertain, and may be heated in contact with water residues for many hours without suffering any development of interfering colors, and is far less sensitive to the interfering action of the substances causing errors than when the old standard reagent is used.

Complete sulfonation usually takes place in from thirty minutes to one hour, but the time of heating suggested is to absolutely insure the absence of even a trace of mono acid. The proportion of acids given is such that the viscosity of the final product is sufficiently low to permit measuring the reagent from a 2 cc. pipet and also prevent the solidification of the reagent should the temperature of the laboratory fall to a little below 15°.

It has been tested during the past year in our student laboratories in large classes and appears to be a great improvement over the reagent commonly employed.

Theoretically 2 cc. of this new reagent should be capable of taking up 297 parts per million of nitrogen as nitrate. But on trial it has been found that the results are not always reliable when over 50 parts per million are treated and serious discrepancies arise should the nitrate content be over 80 parts per million. The old reagent is in this respect much worse.

Determination of Nitrates in Water.—First determin the alkalinity, the chlorine and nitrite content and the color of the sample. Should the color be high decolorize with "aluminium cream."

Measure into an evaporator 100 cc. of the sample, or if the nitrates are very high, such a volume as will contain about 10 parts per million of nitric nitrogen, fairly low colorimeter readings having been found most reliable. Add sufficient 0.04 *N* or 0.02 *N* sulfuric acid to not quite neutralize all the alkalinity, then a volume of standard solution of silver sulfate free from nitrate (4.3969 grams per liter, 1 cc. = 1 cc. of standard silver nitrate solution = 1 mg. Cl per cc.), which will precipitate all but about 0.5 mg. of the chlorine. Heat to boiling, add a little "aluminium cream," filter and wash with small amounts of hot water. Evaporate the filtrates to dryness, add 2 cc. of the disulfonic acid reagent, rubbing with a glass rod to insure intimate contact. Should the residue be compact or vitreous in appearance from much magnesium or much iron present, place the evaporator on the water bath for a few minutes. Dilute with distilled

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water and add slowly a strong solution of potassium hydroxide (10–12 normal) until the maximum color is developed. Transfer to a colorimeter cylinder, filtering, if necessary, and compare with a potassium nitrate or tripotassium nitrophenoldisulfonate standard.

Should nitrites be present in excess of 1 part per million of nitrogen a slight error will be introduced. They should therefore be removed by heating the sample a few moments with a few drops of hydrogen peroxide[1] (free from nitrates) repeatedly added or dilute potassium permanganate may be added in the cold until a trace of pink appears, and a correction applied to the final nitrate nitrogen reading due to the conversion of the nitrites to nitrates.

Permanent Standards.—Permanent standards made according to the method of the American Public Health Association[2] using the reagent suggested above, or a series of standards using tripotassium nitrophenoldisulfonate may be employed.

The use of permanent standards with the reagent suggested, containing as it does no mono acids, introduces no errors, since the reagent does not change its composition with age, the color of the final product is not influenced by heat, nor by moderate variation in volume of reagent or volume of alkali used. Nor does dilution change the relative value of the standards.

Preparation of Tripotassium Nitrophenoldisulfonate, $C_6H_2OK(SO_3K)_2NO_2$. —The pure salt isolated in the progress of the investigation of the nature of the compound producing the yellow color proved so valuable as a standard for the study of sources of error that much time was spent in an attempt to discover a convenient method for its preparation. None of the methods given in the literature of the nitrophenolsulfonic acids proved successful. As a warning to future investigators it should be recorded that every attempt to sulfonate *o*-nitrophenol with fuming sulfuric acid at 100° resulted in violent explosions. Treatment with fuming acid in the cold for twenty-four hours causes the splitting off of the nitro group and an impure phenoldisulfonic acid results.

The only method that has proved practicable thus far in our hands consists in adding, in the cold, to the disulfonic acid reagent, described above, the theoretical amount of dry finely powdered potassium nitrate in very small pinches at a time (for every cubic centimeter of reagent 0.1076 gram of potassium nitrate), stirring thoroughly after each addition. The product is then diluted, treated with dry barium carbonate until a deep yellow color results, filtered, and the precipitate washed with boiling water to dissolve the barium nitrophenoldisulfonate which is but sparingly soluble in cold water. Much of the product sought is lost unless the

[1] Tatlock and Thompson, *J. Soc. Chem. Ind.*, 23, 428 (1904).

[2] *J. Infect. Dis.*, 1905, May Sup., 41. Jackson, *Tech. Quart.*, 13, 320 (1900).

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extraction with boiling water is thorough. Filtrates and washings are united, the barium removed by adding potassium carbonate until alkaline, the solution filtered and the filtrate concentrated to crystallization. The yield obtained is about 60 per cent. of the theoretical. The salt may be easily purified by recrystallization from water. This method is suggested provisionally until a better one has been devised.

To prepare the standards, the recrystallized salt thus obtained is dissolved in distilled water and the solution compared in a colorimeter with a known weight of potassium nitrate treated with the reagent in the usual manner. From the value obtained the proper dilutions for a series of standards are calculated.

Carrying the purification of the tripotassium salt to a point where the theoretical amounts might be weighed out for a set of standards is not recommended, since the products must be dried in a current of carbon dioxide.[1]

Standards prepared as above described were checked repeatedly, both with the C. P. salts and with potassium nitrate standards, during many months and have as yet shown no tendency to change. During most of this period they have stood in clear glass bottles in diffused daylight. The authors therefore believe that such standards may be recommended as convenient, reliable, and as doing away with the very strongly alkaline standards formerly employed.

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NOTE.

A Simple Hydrogen Sulfide Generator.—Many generators have been devised for hydrogen sulfide and I offer no apology for adding one to the number. Chemists have suffered so much at the hands of this bad-smelling gas that they will be ready to welcome anything which promises to alleviate their discomfort. The simple apparatus which I here submit will be of great service in small laboratories and to chemists who want moderate quantities of the gas from time to time at a moment's notice.

There are two principles involved in the various forms of hydrogen sulfide generators. In the one the acid in bulk is applied to the sulfide repeatedly, thus becoming weaker and weaker, and must finally be removed before it is fully exhausted. This is the principle of the long used and popular Kipp generator. In the other form a small quantity of acid is applied to a large quantity of the sulfide and when spent flows away automatically. This is the principle of the generators of Parsons, Dudley and others and is the one used in the apparatus here described.

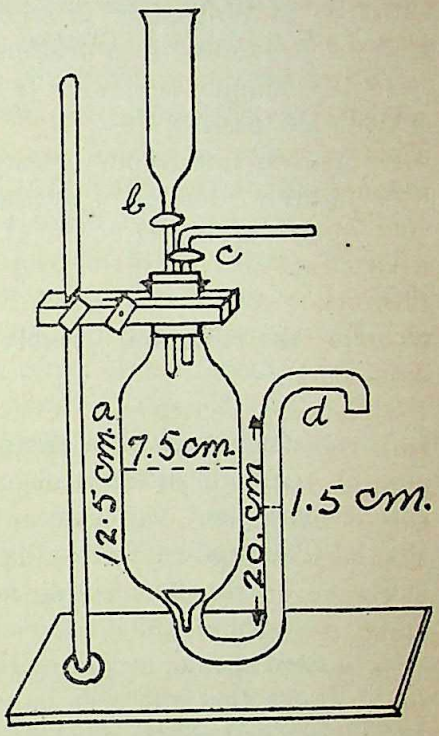
The sulfide is placed in the body (*a*) of the apparatus. The acid, best

[1] THIS JOURNAL, 32, 635 (1910).

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hydrochloric acid, is admitted from the funnel tube through the stopcock (*b*), just enough to serve the purpose, generally a few drops. The gas passes out through the delivery tube (*c*) which may be connected with a wash bottle if desirable. On closing the stopcock in the delivery tube, the acid is driven away from the sulfide up the waste tube and the excess overflows at (*d*) into a bottle or through a rubber tube to the sink or to the outside air. The apparatus is placed in a convenient support and can be carried from place to place with perfect ease.



The waste tube is 20 cm. long, which gives pressure enough for ordinary purposes. If a greater pressure is desired, the tube can be closed with a cork, or lengthened with rubber. The apparatus is equally well adapted to the generation of hydrogen or carbon dioxide.

The advantages of this apparatus are as follows:

1. The quantity of acid in the generator is always small, generally less than 50 cc.

2. If the acid is added drop by drop and not in large excess, it will be practically exhausted before it passes out through the waste tube.

3. When the stopcock is closed in the delivery tube, the acid is driven away from the sulfide at once and the generation of the gas ceases. At most only a few bubbles pass out and these go through the waste tube into the outer air.

4. No large quantity of gas is in the apparatus to be wasted by the student in passing it rapidly through his solution.

5. The apparatus cleans itself, being emptied every time the stopcock in the delivery tube is closed. To wash out admit water through the funnel and force it out through the waste tube by blowing into the delivery tube.

6. It is simple, cheap, always ready, wastes no gas, if properly treated needs no attention except when it must be refilled.

The apparatus was made for me by Eimer & Amend, of New York. I have had one in use for four months with perfect satisfaction.

J. I. D. HINDS.

UNIVERSITY OF NASHVILLE. NASHVILLE, TENN.,
January, 1911.

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[From the Department of Experimental Medicine, Parke, Davis & Co., Detroit, Mich.]

TRIBROMO-*tert*-BUTYL ALCOHOL, $C_4H_7OBr_3$.[1]

By T. B. Aldrich.

Received December 29, 1910.

In 1881 C. Willgerodt[2] in studying the action of caustic alkalies on a mixture of chloroform in acetone obtained a crystallin compound which resembled camphor somewhat in odor and taste and consequently excited considerable interest.

By analysis and vapor density determinations it was shown that it is an addition product of acetone and chloroform, having the formula $C_4H_7OCl_3$ or $CHCl_3.(CH_3)_2CO$. It was given the name acetone chloroform and later[3] the structural formula $CCl_3—\overset{CH_3}{\underset{CH_3}{|}}COH$, showing it to be trichloro-*tert*-butyl alcohol or the trichloride of acetonic acid. The melting point of trichloro-*tert*-butyl alcohol which has received the commercial name "chloretone," varies according to the amount of water associated with it. The product recrystallized from solvents containing water and allowed to dry in the open air has a melting point near 80°. The anhydrous compound which Cameron and Holly[4] claim has probably never been obtained should, according to them, melt near but above 97°. Willgerodt[5] states that the acetone chloroform described by him, when recrystallized from dilute alcohol and ether, melted at 80–81° and contained exactly 0.5 molecule of water; whereas the product crystallized from carbon disulfide or repeatedly sublimed is anhydrous and melts at 96°.

The following are some of the properties of chloretone. Boiling point 167° (uncorrected), very volatil in the air, readily volatilized with steam. It has a camphorous odor and taste. It is sparingly soluble in water (0.5 per cent.); extremely soluble in ether, alcohol, glacial acetic acid, acetone and chloroform. Soluble also in white neutral oil, and vegetable oils and fats. It is widely used as a therapeutic agent.[6]

I have mentioned these facts relative to chloretone, its manner of formation, etc., in order to compare it with the analogous compound, tribromo-*tert*-butyl alcohol, or "brometone."

[1] "Brometone" is the commercial name.

[2] *Ber.*, 14, 2451 (1881).

[3] *Ibid.*, 15, 2305 (1882).

[4] *J. Phys. Chem.*, 2, 322 (1898).

[5] *Ber.*, 16, 1585 (1883).

[6] Houghton and Aldrich, *J. Am. Med. Assoc.*, Sept. 23, 1899, p. 77; also *Am. J. Physiol.* (Proceedings), 3, 26 (1900).

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This compound is prepared in a similar manner to chloretone, that is, by the action of solid caustic alkalies on a mixture of acetone and bromoform; but it is more difficult to isolate in a pure form. In making chloretone any excess of chloroform can be readily blown off or distilled off. This can be done, but not so readily, with an excess of bromoform and not without considerable loss of the product desired. It can be obtained, however, as a beautiful white crystallin compound, by removing the excess of bromoform, distilling with steam and recrystallizing from a suitable solvent.

It melts at 167–176°, volatilizes in the air but much more slowly than the corresponding compound. At attempt to distil it at ordinary pressure caused decomposition and the evolution of a very irritating gas. No attempt was made to distil it under reduced pressure. It has a camphorous odor and taste. Its solubilities are very similar to those of chloretone. There is no doubt that we have here tribromo-*tert*-butyl alcohol, or the tribromide of acetonic acid, shown by the following analyses which were carried out with a product crystallized from dilute alcohol a number of times and dried in a desiccator over calcium chloride.

	Calculated for $C_4H_7CBr_3$.	Found. 1.	2.	3.	4.	Average.
C	15.43	15.31	15.24	16.13	15.26	15.48
H	2.25	2.37	2.26	2.33	2.41	2.34
O	5.15	...	...	...	...	...
Br	77.17	76.24	75.44	76.84	76.24	76.19

The following analyses were also made from another product dried over calcium chloride, the last two after long drying:

	Calculated for $C_4H_7OBr_3$	Found. 1.	2.	3.	4.	Average.	6.	7.
C	15.43	15.21	14.58	...	..	14.90	15.7	15.37
H	2.25	2.19	2.18	...	..	2.19	2.32	2.31
Br	77.17	76.92	76.26	76.58	77.1	76.72	77.06	77.14

The above analyses and the difficulty of obtaining very closely concordant results would indicate that there is a varying amount of water present in brometone, this being indicated by the carbon and bromine content, which are low, and the hydrogen content, which in general is high.

The analyses are however, sufficiently near to assign to it the formula $C_4H_7OBr_3$ and it has no doubt the structural formula $CBr_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{COH}}}}$ similar to that assigned to chloretone by Willgerodt.

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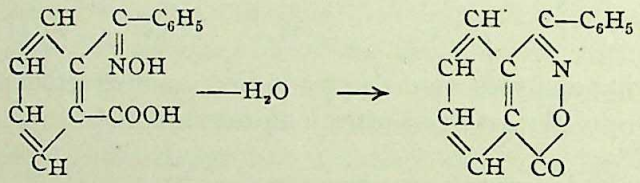
Several attempts have been made to obtain acetonic acid from this product as Willgerodt did from chloretone, but although a small amount of a supposedly organic acid was obtained and an attempt made to convert it into the barium salt, the amount was so small that the results obtained were not sufficiently close to demonstrate its formation, although it was probable. What has been said relative to chloretone (Cameron and Holly) is no doubt true of brometone, *viz.*, that the substance contains water, and in varying amounts, that the water cannot be detected or eliminated by mechanical means, that it is not present to form a hydrate. Therefore it is present to form a solid solution. Brometone is used as a therapeutic agent. For its pharmacological action see Houghton and Aldrich.[1]

THE REDUCTION OF THE ANHYDROXIME OF *o*-BENZOYL-BENZOIC ACID.

By Robert Evstafieff Rose.

Received January 7, 1911.

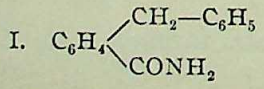
In common with other oximes of aromatic aldehydes and ketones containing a carboxyl group in the *o*-position to the carbonyl that of *o*-benzoylbenzoic acid is incapable of existing in the free state. It loses the elements of water spontaneously when liberated from its alkali salt, yielding what may be termed an anhydroxime thus:

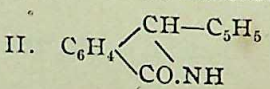


Several representatives of this class of compounds are known, but their chemical behavior has been little studied, though a closely related substance, the oxime of phenolphthalein, has been the subject of thorough investigation. It therefore seemed of interest to examin the behavior of the anhydroxime of *o*-benzoylbenzoic acid more especially towards reducing agents, the analogous compound obtained from phenolphthalein having proved to be readily reducible.

Experiment showed the anhydroxime to undergo quantitative reduction when treated with nascent hydrogen, a stable crystallin reduction product being formed.

For this substance the following formulas must be considered:





of which the first shows the reduction product as the amide of *o*-benzyl-

[1] *Am. J. Physiol.* (proceedings), 8, 18 (1903).

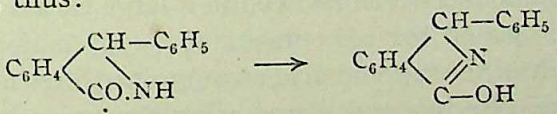
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benzoic acid, while the second represents the substance as the lactam of the *o*-carbonic acid of diphenylmethylamine. Formula I, though appearing somewhat improbable when compared with that given above for the anhydroxime, deserves consideration because it is analogous to the one originally proposed by R. Meyer[1] for the reduction product of the oxime of phenolphthalein. Study of the behavior of the compound and the analytical results obtained led the author to adopt the alternative formula II as being more closely in accord with the observed facts. Did formula I represent the structure of the substance then as an acid amide it should be capable of undergoing hydrolysis to the corresponding acid; this is not the case. Moreover the percentage difference in carbon and hydrogen in the two compounds amounting as it does to 0.76 per cent. and 0.90 per cent. respectively is quite sufficient to allow of analytical determination, and the values found agree closely with those calculated for the lactam. Again, a substance possessing the constitution represented by formula II should be extremely stable, and the reduction product does, in fact, resist the action of reducing and hydrolyzing agents to a remarkable degree. Thus it dissolves readily in concentrated sulfuric acid from which it is precipitated in an unchanged condition on the addition of water, while if the acid solution is heated sulfonation alone results.

The substance is insoluble in alkalies; behavior which is in conformity with the lactam structure since this represents the compound as being more basic than acidic. As was to be expected the reduction product readily undergoes acetylation, yielding a monoacetyl derivative.

Further evidence is furnished by the behavior of the compound toward reagents for the hydroxyl group. It is itself colorless, but when treated with phosphorus pentachloride, acetyl chloride, or benzoyl chloride yields a dark blue-green, highly fluorescent substance which was not obtained in a state of purity. This change to a highly colored compound can be satisfactorily explained on the assumption that the action of these reagents causes tautomerism to the lactam, the chromophore —C=N— being produced; thus:



The constitution of this product is of interest because of its probable analogy to the corresponding derivative of phenolphthalein oxime which will form the subject of a subsequent paper.

Experimental.

Preparation of the Oxime of o-Benzoylbenzoic Acid.[2]—22.6 grams *o*-benzoyl-

[1] *Ber.*, 40, 1454.

[2] See Thorpe, *Ber.*, 26, 1262, 1795.

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benzoic acid, melting point 93–96°, were dissolved in a solution of 56 grams potassium hydroxide in 200 cc. water and to this were added 15.75 grams hydroxylamine hydrochloride in concentrated aqueous solution. The reaction mixture was boiled during 20 minutes, allowed to stand 12 hours at room temperature, then acidified with hydrochloric acid; a crystallin mass separated which was recrystallized from ethyl alcohol; melting point 161–163. Yield, 90 per cent.

Reduction of the Anhydroxime.—Ten grams of the substance were dissolved in the minimum quantity of glacial acetic acid and a large excess of zinc dust added in small portions. Slight warming was sufficient to start the reaction after the addition of the first portion of zinc, the remaining metal being thereafter added in such a manner as to keep the mixture near the boiling point. When all the zinc had been added the reaction mixture was allowed to stand for half an hour, then poured into cold water. The product was recrystallized from 75 per cent. acetic acid. It melts at 218–220°, and was found to be rather soluble in methyl and ethyl alcohols, slightly soluble in ether, and insoluble in petroleum ether. Analysis gave the following results:

Found: C, 80.33, 80.05; H, 5.29, 5.46; N, 6.70.
Calculated for $C_{14}H_{11}NO$: C, 80.38; H, 5.26; N, 6.69.

A molecular weight determination in acetic acid by the cryoscopic method gave the value 221 instead of that calculated 209.

Acetylation of the Reduction Product.—Two grams of the compound were dissolved in 30 cc. of acetic anhydride to which 4 grams of anhydrous sodium acetate had been added and the mixture boiled for 6 hours. On pouring the reaction mixture into cold water a solid separated, which, after recrystallization from aqueous acetic acid, melted constantly at 153–155°. Analysis gave:

N, 5.60; calculated for $C_{16}H_{13}O_3N$: N, 5.57.

Sulfonation of the Reduction Product.—In an endeavor to hydrolyze the substance it was treated with concentrated sulfuric acid; it dissolved readily in the acid but was reprecipitated unchanged on dilution. When 5 grams of the compound were dissolved in a large excess of concentrated sulfuric acid and heated for 4 hours at 160–170° sulfonation resulted, and the barium salt of the sulfonic acid was obtained after neutralizing with barium carbonate, filtering and evaporating the aqueous solution. The salt crystallized from water in small prisms containing two molecules of water of hydration. Analysis gave the following results:

Found: H_2O, 4.24; Ba, 18.26.
Calculated for $(C_{14}H_{10}O_4NS)_2Ba.2H_2O$: H_2O, 4.25; Ba, 18.29.

Action of Benzoyl Chloride and Acetyl Chloride on the Reduction Product.—No satisfactory results were obtained by the use of these reagents; in every case the reaction mixture became dark blue-green in color with

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the formation of a substance far more soluble in ether and benzene than the original compound. It is proposed to examin this reaction further.

Distillation of the Reduction Product with Zinc Dust.—An attempt was made to reduce the substance still further by distilling with zinc dust, this method having been used by v. Baeyer in converting oxindole into indole; as a result an oily mixture of substances was obtained from which colorless leaflets separated which were found to be carbazole. The oily substance formed at the same time showed most intense blue-red fluorescence but was present in quantities too small to admit of identification.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE.]

THE ACTION OF ETHYL ALCOHOL ON PARATOLUIDINE DIAZONIUM HYDROCHLORIDE AND OF SULFURIC ACID ON THE ETHYL ETHER OF PARACRESOL.

BY PERCIVAL RUDOLPH ROBERTS AND GELLERT ALLEMAN.

Received January 2, 1911.

Some years ago, one of us[1] studied the action of methyl alcohol on paratoluidine diazonium sulfate and the effect of sulfuric acid on the methyl ether of paracresol. It was thought that the ethyl ether of paracresol could be obtained in a like manner, and with no more difficulty than attended the preparation of the corresponding methoxy compound. Numerous failures to secure a good yield of the ethoxy product led to changes in the methods and conditions incident to the production of the material desired. Owing to the fact that paratoluidine sulfate is much less soluble in ethyl alcohol than is paratoluidine hydrochloride, the latter compound was employed.

Preparation of the Diazonium Compound.—Two hundred grams of Kahlbaum's paratoluidine were melted in 400 cc. of hot water, and 400 cc. of fuming hydrochloric acid gradually added. During the addition of the acid, the mixture was stirred in order to dissolve the hydrochloride formed. As soon as complete solution took place, the material was cooled by immersing the beaker containing it in cold water. The paratoluidine hydrochloride separated, on cooling, in perfectly white crystals. The supernatant liquid was decanted, the crystals thrown on a funnel fitted with a platinum cone, and the adhering water and acid removed by filtering under diminished pressure. The crystals were then placed on an unglazed porcelain plate to facilitate drying. They were used within an hour of the time they were removed from the liquid, because the color of the crystals changed, on standing over night, which indicated that, within a short time, some decomposition resulted. The crystals, which

[1] Alleman, *Am. Chem. J.*, 31, 24 (1904).

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were slightly moist, were dissolved in 99 per cent. ethyl alcohol, and the resulting solution placed in tall, narrow gas-washing bottles, holding about 500 cc. Two cylinders were connected in series. They were then packed in a mixture of ice and salt and cooled to —25°. Nitrogen trioxide, generated by treating lump arsenic trioxide with nitric acid of 1.35 sp. gr., was first cooled by passing it through two gas-washing bottles surrounded by ice water, and then conducted into the bottles containing the alcoholic solution of the paratoluidine hydrochloride. During the passage of the gas, the temperature of the latter named solution was not permitted to rise above —15°. This was easily regulated by closely watching the supply of the entering gas, and by a liberal use of ice and salt. Within twenty minutes the alcoholic solution turned red, and the diazotization was completed in about one hour—the time depending upon the rapidity of the flow of nitrogen trioxide. The end of the reaction could be easily determined by removing a small portion of the alcoholic solution and adding a solution of sodium hydroxide to it. In case the hydrochloride had not been completely diazotized, a distinct odor of paratoluidine was noticed after the addition of an excess of the sodium hydroxide solution. Frequently, at the end of the diazotizing process, a separation of two distinct liquids was noticed in the gas-washing bottle. This was especially noticeable when the temperature was kept very low and a large amount of nitrogen trioxide passed through the solution. On examination, the top layer was found to be composed of ethyl nitrite, but it was noticed also that the formation of this layer was always indicative of a larger yield of the desired product than could be obtained when the formation of the ethyl nitrite did not take place. The diazotized material did not separate from the alcohol at —25° and no attempts were made to precipitate it.

Decomposition of the Diazonium Compound.—The whole solution was transferred to a five-liter balloon flask connected with a long condenser, the balloon flask placed on a steaming water bath, and the decomposition of the diazonium compound immediately begun. The first noticeable change was in color; the light transparent wine-red solution changed to one dark and opaque. Then the solution began to foam, the foam being white for a few minutes, after which this first reaction apparently lessened in intensity for a short time. A second and much more violent reaction followed, and the color changed to a green-black. Frequently the decomposition had to be checked by pouring cold water on the balloon flask, or the whole solution would be lost through the condenser tube. Several fires resulted from the ignition of the alcohol, which was shot out of the condenser tube on certain occasions, and others from the alcohol scattered in consequence of flasks broken from sudden shock during the too rapid decomposition of the diazo compound. Fires were

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subsequently prevented by extinguishing all the flames in the room in which the decomposition was effected as soon as it was well under way. The decomposition was completed in about twenty minutes. The solution was then boiled for twenty minutes, after which the return condenser was replaced by a Hempel tube 1 meter long, the latter connected with a condenser, and the excess of alcohol distilled off. Considerable toluene passed over with the alcohol and the last portion had a distinct odor of ethyl ether. The residue in the balloon flask was then mixed with five times its volume of water. A dark oil separated, and the whole was heated and subjected to distillation with steam. A light lemon-yellow oil passed over and was condensed with the water in which it is practically insoluble. The oil was separated from the water by means of a separating funnel, and transferred to a flask containing fused calcium chloride. After drying for three days in this manner, it was filtered through glass wool into a distilling bulb, and fractioned. This oil has an intensely sweet and penetrating odor. It stains the skin yellow, and, after a time, on exposure to air, the odor changes and is suggestive of fresh horse manure. The average yield was about 35 per cent. of the theoretical.

After three distillations, 698 grams of oil were obtained, which boiled between 185° and 195°. 455 grams of the above distilled between 185° and 191° and 360 grams between 187° and 191°. The latter material was made use of in the following experiments. The refractive index of the latter fraction at 15° was 1.51069. The oil is very soluble in methyl alcohol, ethyl alcohol, ether, toluene and benzene. It is lighter than water.

This is evidently the paraethoxytoluene obtained by Engelhardt and Latschinow.[1]

Paraethoxymetatoluenesulfonic Acid.—Two hundred grams concentrated sulfuric acid were added to 100 grams of the paraethoxytoluene. A slight change in color, and the development of considerable heat, indicated that a reaction had taken place at the ordinary temperature, and without the application of heat. After three hours, on cooling, yellow crystals were obtained. These were removed from the solution, placed on a porous draining plate, and dried. The material was afterwards crystallized from absolute alcohol, in order to free it from any unchanged paraethoxytoluene and free sulfuric acid. From the alcoholic solution, beautiful, transparent, colorless crystals were obtained. They suggest hopper-shaped salt crystals; however, they are not isometric, but probably monoclinic. Crystals 1 cm. by 2 mm. were obtained. They melt sharply at 92–92.5°. The method just indicated furnishes a purer sulfonic acid than was obtained by first making the barium salt of the acid and then

[1] *Z. für Chem.*, 1869, 619.

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obtaining the free acid from the latter. The free sulfonic acid is extremely soluble in water, methyl alcohol, ethyl alcohol, and acetone. It is practically insoluble in ether, chloroform, carbon tetrachloride, benzene, benzine, toluene and ligroin.

The properties of the sulfone chloride and sulfonamide indicate that the sulfonic acid group enters in the meta position.

Salts of p-Ethoxytoluenemetasulfonic Acid. Barium Salt, $(C_6H_3(CH_3)(OC_2H_5)(SO_3))_2Ba.4H_2O$.—The mixture of the monosulfonic acid and sulfuric acid was dissolved in water, heated, neutralized with barium carbonate, and filtered to remove the barium sulfate. The barium sulfonate crystallizes in large flakes which are lustrous and suggest, in appearance, boric acid. On standing during the summer vacation, the solution evaporated, leaving crystals of the barium sulfonate about 3 cm. in length and 1 cm. in thickness. The salt does not effloresce on long exposure to air. After repeated crystallization of this salt, the following results were obtained, on analysis:

Calculated for $(C_9H_{11}O_4S)_2Ba.4H_2O$: Ba, 21.48; H_2O, 11.26.
Found: Ba, 21.47, 21.45; H_2O, 11.22, 11.26.

The barium salt is quite soluble in cold water.

A large quantity of the pure free acid was obtained by exactly precipitating the barium in the barium salt of the sulfonic acid by means of dilute sulfuric acid.

Potassium Salt, $C_6H_3(CH_3)(OC_2H_5)SO_3K.H_2O$.—This salt was prepared by exactly neutralizing a hot aqueous solution of the free sulfonic acid with potassium carbonate. Large transparent, colorless monoclinic prisms were obtained, some being 4 cm. long and 4 mm. in thickness. The salt does not effloresce on long exposure to air. It is quite soluble in water.

Calculated for $C_9H_{11}O_4SK.H_2O$: K, 14.32; H_2O, 6.59.
Found: K, 14.43, 14.21; H_2O, 6.62, 6.71.

Sodium Salt, $C_6H_3(CH_3)(OC_2H_5)SO_3Na.H_2O$.—The sodium salt was made from the free sulfonic acid by exactly neutralizing an aqueous solution of the acid with sodium carbonate. Distinct colorless monoclinic prisms 6 mm. by 3 mm. by 2 mm. separated. The salt is quite stable and does not effloresce upon exposure to air. It is quite soluble in water.

Calculated for $C_9H_{11}O_4SNa$: Na, 9.00; H_2O, 7.03.
Found: Na, 8.93, 9.07; H_2O, 7.10, 7.13.

The salt, when heated for a long time, readily decomposes at a temperature slightly higher than 125°.

Calcium Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Ca.7H_2O$.—The calcium salt was prepared by neutralizing a boiling aqueous solution of the free acid with finely powdered Iceland spar. Yellow-white, transparent glistening

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needles separated, which, on recrystallization, lost their yellow tinge. The salt is moderately soluble in water and is quite stable on exposure to air.

Calculated for $(C_9H_{11}O_4S)_2Ca.7H_2O$:	Ca, 6.72;	H_2O, 21.13.
Found:	Ca, 6.74, 6.63;	H_2O, 21.18, 21.03.

Zinc Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Zn.6H_2O$.—Zinc oxide was added to a hot aqueous solution of the free sulfonic acid. After filtering off the excess of zinc oxide and evaporating, white needles separated. These crystals are stable in air. When crushed between the fingers, they have a greasy feeling suggestive of zinc stearate.

Calculated for $(C_9H_{11}O_4S)_2Zn.6H_2O$:	Zn, 10.83;	H_2O, 17.90.
Found:	Zn, 10.82, 10.93;	H_2O, 17.77, 18.07.

Nickel Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Ni.5H_2O$.—The nickel salt was made by neutralizing the free sulfonic acid with nickel carbonate. It forms small well defined crystals which have a very slight light green tint. The salt is stable when exposed to air. Difficulty was experienced in the determination for water as it apparently decomposes about the time it loses its last trace of water.

Calculated for $(C_9H_{11}O_4S)_2Ni.5H_2O$:	Ni, 10.13;	H_2O, 15.55.
Found:	Ni, 10.11, 10.16;	H_2O, 15.48, 15.58.

Copper Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Cu.6H_2O$.—In preparing this copper salt by treating the free acid with freshly prepared copper oxide, a peculiar effect was noticed. The copper oxide was entirely free from alkali but when the black oxide was added to the free acid and the mixture heated, the black oxide of copper changed to a slate color, and the latter did not subsequently dissolve. The copper salt crystallizes in distinct unattached monoclinic prisms 15 mm. by 5 mm. by 3 mm. The twin crystals were much larger. The crystals are perfectly transparent, almost colorless, with a suggestion of a blue tinge.

Calculated for $(C_9H_{11}O_4S)_2Cu.6H_2O$:	Cu, 10.57;	H_2O, 17.95.
Found:	Cu, 10.96, 10.71, 10.44;	H_2O, 18.00, 18.02, 18.07.

Copper Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Cu.12H_2O$.—Another copper salt was made by precipitating the barium from the barium salt by means of copper sulfate. Light bluish needles were obtained, which were readily soluble in water.

Calculated for $(C_9H_{11}O_4S)_2Cu.12H_2O$:	Cu, 8.95;	H_2O, 30.44.
Found:	Cu, 8.77, 8.82;	H_2O, 30.42, 30.39.

Lead Salt, $(C_6H_3(CH_3)(OC_2H_5)SO_3)_2Pb.6H_2O$.—Made by neutralizing the free acid with freshly prepared lead hydroxide. Large white crystals were obtained, which on exposure to air lost their luster, without apparently losing water of crystallization. The salt strongly suggests a change in crystal system on exposure to air as in the case of crystals of sulfur.

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Calculated for $(C_9H_{11}O_4S)_2Pb.6H_2O$: Pb, 27.72; H_2O, 14.48.
Found: Pb, 27.76, 27.57; H_2O, 14.53, 14.69.

All of the above salts have a much stronger crystallizing force and are much less soluble in water than the corresponding salts of paramethoxy-metatoluenesulfonic acid prepared and described by Alleman.[1]

We are indebted to Mr. R. L. Hill, of this laboratory, for assistance in connection with the purification and analysis of the lead and copper salts.

The evidence showing that the sulfonic acid entered in the meta position will be presented in a subsequent paper.

SWARTHMORE, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

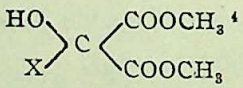
CONDENSATIONS IN THE MESOXALIC ESTER SERIES.

BY RICHARD SYDNEY CURTISS AND EARLE K. STRACHAM.

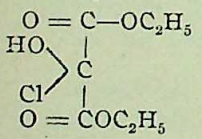
Received January 19, 1911.

The methods hitherto used for making ethyl oxomalonate, $O = C = (CO_2C_2H_5)_2$, have given a product which is a mixture of this substance with ethyl dihydroxymalonate. To produce the former substance in a state of purity it is necessary to distil ethyl dihydroxymalonate with phosphorus pentoxide.[2] Thus we have prepared this substance, a very reactive green oil, and have studied its carbonyl reactions, following them by the interesting, and more or less rapid change of color.[3]

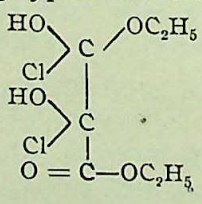
We have first investigated the action of dry hydrochloric and hydrobromic acid gases on ethyl oxomalonate. These substances react readily at a low temperature, giving colorless, crystallin products. This keto ester differs from the methyl ester which gave well defined, but very unstable crystallin addition products of the haloid acids on the ketone double bond, thus:



in that it appears to be more reactive and to yield a mixture of the mono-, di- and trihaloid acid addition products. These are probably correctly represented by the following typical formulas:

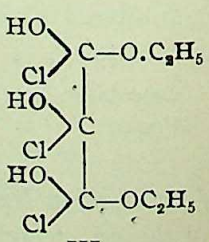


I.



II.

and



III.

[1] *Am. Chem. J.*, 31, 24 (1904).
[2] See Curtiss and Spencer, THIS JOURNAL, 31, 1054.
[3] *Ibid.*
[4] *Ibid.*, 31, 1055.

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Our reasons for assigning this structure in Formula I, as opposed to that of an oxonium salt on the α-carbonyl oxygen, were briefly discussed in the paper referred to above. That the second and third molecules of acid may add on the carboxyl oxygen as oxonium salts, we are not prepared to deny. The addition products herein described are very unstable and experiments have shown that the haloid acid slowly dissociates from them even at the low termperature of an ether-carbon-dioxide freezing mixture (about —60 to —70°). When melted, they form thick, colorless liquids, which then give off the acid gas rapidly below zero, while the green color of the original keto ester returns. These compounds are to be utilized in organic syntheses.

Further, we have studied the action of some acid amides on this ketone ester. Urethan and urea react vigorously and yield colorless, crystallin products. The analysis of the ethylurethan derivative shows that the intermediate addition product on the carbonyl double bond was formed, $C_2H_5O.CO.N.C.(OH) : (COOC_2H_5)_2$. This compound gives
H
a disodium salt when treated with metallic sodium. An attempt was made to remove the elements of water from this addition compound to produce the $N = C<$ double bond and chromophore group. A crystallin compound was formed which melted at 121.5°. It was, however, colorless.

The analysis of the condensation product of urea with ethyl oxomalonate shows that an unstable addition compound is apparently formed:

$$NH_2.CO.NH.C.(OH) : (COOC_2H_5)_2$$

with one of the amine groups.

Experimental.

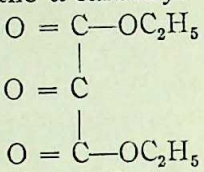
Ethyl Oxomalonate.—Twenty-five grams of ethyl dihydroxymalonate were mixed with 23 grams (1.25 molecules) of phosphorus pentoxide in a distilling flask. After fifteen minutes a green oil appeared. At the end of three hours the mixture was distilled under reduced pressure. It boiled quite constantly at about 122° at 40 mm. (uncor.); yield, 21.1 grams or 90.5 per cent. A larger yield, 94 per cent., was obtained when the ketone ester was extracted from the reaction mixture by sodium-dry ether before distilling. The ester boiled at 117° under 31 mm.

Ethyl oxomalonate is a green oil, slightly more yellow than the corresponding methyl compound. Its density at 20°/20° is 1.119. When chilled in a mixture of solid carbon dioxide and ether, it crystallizes completely, in balls of colorless radiating plates. The crystals melt below —30°.

Action of Hydrochloric Acid Gas on Ethyl Oxomalonate.—One gram of ethyl oxomalonate was placed in a well stoppered flask provided with a calcium chloride tube, and cooled to —60° to —70°. Dry hydro-

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chloric acid gas was passed into the flask. The green color of the ester soon disappeared and a thick colorless syrup resulted. The loss of color indicated saturation of the α carbonyl double bond, which plays its part as a chromophore in α  , and, as shown in the reaction with the methyl ester,[1] is the first point of attack by the acid. The viscous syrup soon solidified to a white crystallin mass, which slowly melted between —29° and —10°, with the evolution of hydrochloric acid.

For analysis, 1.0250 grams of ethyl oxomalonate were exposed to a stream of the acid gas for half an hour, during which time the colorless, crystallin product was thoroughly ground until it formed a fine, dry powder, by means of a glass rod which had previously been fitted to the rubber stopper of the flask.

The combined hydrochloric acid was determined by inverting the flask in a beaker of water, removing the stopper, and allowing the water to enter the flask. Water instantly decomposes the product. The solution was titrated with standard alkali. Correction was made for the gaseous hydrochloric acid in the flask.

1.0250 g. gave 0.4984 g. HCl, equivalent to 2.32 molecules.
1.2152 g. gave 0.6091 g. HCl, equivalent to 2.39 molecules.

The fact that hydrochloric acid readily dissociates from these compounds even at —60° is shown by the following experiments. Dry carbon dioxide gas was passed for fifteen minutes through the apparatus containing the dry powdered hydrochloride made as above described. An analysis was then made of the product, and showed the following results:

1. 1.0759 g. gave 0.3430 g. HCl, equivalent to 1.52 molecules.
2. 1.1110 g. gave 0.3963 g. HCl, equivalent to 1.70 molecules.
3. 1.1238 g. gave 0.4125 g. HCl. equivalent to 1.67 molecules.

A second experiment conducted as above, but in which the hydrochloric acid was passed for an excessively long time (2 hours), and then carbon dioxide for five hours, showed on analysis but 0.68 molecule of hydrochloric acid remaining in combination.

0.8864 g. gave 0.1260 g. HCl, equivalent to 0.68 molecule.

In like manner ethyl oxomalonate was saturated with dry hydrobromic acid gas. A crystallin product was obtained which melted in the flask between —21° and —15°. The analysis showed that 2.52 molecules of acid were added.

1.0522 g. gave 1.2760 g. HBr, equivalent to 2.52 molecules.

[1] Curtiss and Spencer, THIS JOURNAL, 31, 1054.

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In three other experiments in which dry carbon dioxide was passed for fifteen minutes through the flask, the analyses showed

1. 1.0692 g. gave 0.9251 g. HBr, equivalent to 1.90 molecules.
2. 0.9937 g. gave 0.9187 g. HBr, equivalent to 1.92 molecules.
3. 1.2723 g. gave 1.0980 g. HBr, equivalent to 1.80 molecules.

Hydrobromic acid, therefore, behaves very similarly to hydrochloric acid under like conditions in these experiments. The additive power of ethyl oxomalonate is shown to be much greater for these acids, than is that of the methyl ester.

Action of Ethylurethan on Ethyl Oxomalonate.—18.5 grams of ethyl-oxomalonate were mixed with a molecular amount (9.46 grams) of urethan. The urethan dissolved slowly in the oxomalonate with a lowering in temperature of 3°. When all was in solution, the temperature rose 25° in ten minutes. As the mixture cooled, the green color of the oxomalonate faded rapidly at first, and in twenty-four hours it had disappeared completely. The viscous, colorless syrup so obtained was crystallized from a mixture of ether and petroleum ether. The crystals melted at 32° to 33° and gave the following figures when analyzed:

Calculated for $C_2H_5O.CO.NH$, $CO_2C_2H_5$ / C / HO, $CO_2C_2H_5$: C, 45.60; H, 6.46; N, 5.32.

Found: C, 45.66, 45.61; H, 6.52; N, 5.46.

Ethyl carbethoxyaminotartronate is easily soluble in alcohol, ether, benzene, and toluene, and slightly soluble in ligroin. It reacts with sodium and yields a disodium salt.

1.25 grams of sodium (1.2 molecules) were added to 5 grams of ethyl carbethoxyaminotartronate dissolved in 15 cc. of sodium-dry ether. The solution became green at once and evolved hydrogen rapidly. Gradually the gas was given off more slowly, and the liquid became darker in color. In three hours the liquid was decidedly brown, and a nearly white salt had separated. This was filtered out, and was washed with dry ether. Yield, 4.91 grams; theory, 5.85 grams. When analyzed the following figures were obtained:

Calculated for $C_{10}H_{15}O_7NNa_2$: Na, 14.98.
Found: Na, 14.80, 14.88, 14.97.

The substance is probably a salt of the enol form of ethyl carbethoxy-aminotartronate, and tautomeric in its reactions.

$$C_2H_5O.OC—N(H)—C(OH)=(COOC_2H_5)_2 + 2Na \longrightarrow C_2H_5OC(ONa)=N—C(ONa)(COOC_2H_5)_2$$

It is easily soluble in water and alcohol, soluble with difficulty in ether, and insoluble in benzene and ligroin. On standing in the air, it becomes pasty, and absorbs carbon dioxide.

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Action of Phosphorus Pentoxide on Ethyl Carbethoxyaminotartronate.—8.5 grams ethyl carbethoxyaminotartronate were mixed with 1.8 grams (1.1 mols.) of phosphorus pentoxide and placed in a tightly stoppered flask and allowed to stand at room temperature for twenty-four hours. The reaction was indicated by a darkening of color of the solution and the formation of a gummy mass. This was filtered, washed with ether, and recrystallized from alcohol. It melted at 121.5°, was colorless, and contained no phosphorus. It was analyzed.

Found: C, 46.97, 47.09; H, 6.53, 6.79; N, 8.62, 8.49.

Neither the analysis nor the lack of color corresponds to ethyl carbethoxyiminomalonate, $C_2H_5O_2C—N = C = (CO_2C_2H_5)_2$, the simple product which might be formed by loss of the elements of one molecule of water. A more complex reaction takes place, and will be further studied.

Action of Urea on Ethyl Oxomalonate.—1.72 grams finely powdered urea were added to 5 grams (1 molecule) of ethyl oxomalonate. The temperature rose quite rapidly to about 60°, and the green color of the keto ester disappeared. The mixture soon solidified. A constant melting point was not obtained, even after repeated recrystallization from ether and alcohol. The substance melted constantly at 132–133° after being three times recrystallized from hot chloroform. But even here as the following analyses show, decomposition apparently takes place during the process of crystallization from hot solutions.

Calculated for $NH_2CO.NH.C.(OH) : (COOC_2H_5)_2$: C, 41.03; H, 5.98; N, 11.96.
Found: C, 40.3, 40.2, 40.7; H, 6.0, 6.1, 5.8; N, 13.8, 13.8.

The figures correspond very closely to those of the primary addition product of urea on the keto ester, containing 5 per cent. of urea. Apparently this addition product, like most of the others we have hitherto made in the mesoxalic ester series, dissociates, when heated, into its constituent parts.[1]

URBANA, ILL.,
January 18, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

KETO ESTER ADDITION PRODUCTS WITH ARYL AMINES AND ALCOHOLS.

BY RICHARD SYDNEY CURTISS, HARRY S. HILL AND R. H. LEWIS.

Received January 23, 1911.

In continuing this line of investigation, which was first worked out on methyl oxomalonate,[2] we have studied the behavior of the three toluidines, aniline, and benzylamine on ethyl oxomalonate, with intent of obtaining

[1] THIS JOURNAL, 31, 1054.
[2] Curtiss and Spencer, *Ibid.*, 31, 1053.

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the intermediate unstable *addition* products. The toluidines react vigorously at low temperatures with the α-ketone group of the ester $O=C=(COOC_2H_5)_2$ and give colorless products of the form $RNH.C.(OH):(COOC_2H_5)_2$, *i. e.*, substituted aminotartronates. These are the primary addition products in the typical reaction of an amine with a ketone group, while the second stage of the reaction gives the final *stable* product $RN:CR_2$ or $(RNH)_2:CR_2$ by elimination of the elements of water.

Aniline, under the same careful manipulation at low temperature, yields only the secondary product of the reaction, ethyl dianilinomalonate, $(C_6H_5NH)_2:C:(CO_2C_2H_5)_2$. The intermediate hypothetical addition product $C_6H_5NH.C.(OH):(COOC_2H_5)_2$ appears too unstable, or too reactive to be separated out even at —15°, and instantly reacts with the aniline as it is added, in preference to the keto group of the ester, and gives the final stable dianilinomalonate. This is in marked contrast to the corresponding reaction of aniline with methyl oxomalonate,[1] where the addition product methyl anilinotartronate, $C_6H_5NH.C.(OH):(CO_2.CH_3)_2$, was obtained as a comparatively stable compound. This, however, easily reacts further with aniline and yields methyl dianilinomalonate, $(C_6H_5NH)_2=C=(CO_2CH_3)_2$.

Benzylamine reacts at —15° with ethyl oxomalonate with loss of color. A colorless, thick syrup results. When this primary addition product is heated it loses the elements of water.

Methyl, ethyl and benzyl alcohols in molecular quantities react with the keto ester. These products are thick, colorless syrups which, like the addition products with the methyl ester, dissociate into the original constituents when heated. They cannot be crystallized or distilled. All these experiments were carried out with thorough exclusion of moisture.

Experimental.

Ethyl Orthotoluidinotartronate.—3.2 grams of orthotoluidine were slowly mixed at —15°, with 5.9 grams of the keto ester (mol. quantities). The temperature rose about 60° while the color soon disappeared. The thick clear liquid soon crystallized. It was purified by recrystallization from ethyl alcohol, and melted without decomposition at 92°.

Calculated for $(CH_3)C_6H_4NH.C.(OH):(CO_2C_2H_5)_2$: C, 59.75; H, 6.81; N, 4.97
Found: C, 59.63 H, 6.67; N, 4.79

Ethyl orthotoluidinotartronate crystallizes in balls of radiating needles. It is easily soluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, and hot ethyl alcohol, and slightly soluble in ligroin and cold alcohol.

Ethyl Paratoluidinotartronate.—3.9 grams of paratoluidine dissolved in 8 cc. of dry ether were slowly mixed with 6.34 grams (1 mol.) of the

[1] To appear in THIS JOURNAL.

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keto ester chilled to —13°. A vigorous reaction took place, heat was evolved, and the color rapidly faded. The mixture had completely solidified in five minutes. The product was recrystallized from absolute alcohol, and analyzed.

Calculated for $(CH_3)C_6H_4NH.C.(OH):(CO_2C_2H_5)_2$: C, 59.75; H, 6.81; N, 4.97.
Found: C, 59.74; H, 6.78; N, 4.96.

Ethyl paratoluidinotartronate is a colorless substance crystallizing in bunches of radiating needles with a melting point of 95°. It is easily soluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, and hot ethyl alcohol. It is slightly soluble in cold alcohol, and ligroin.

These para- and orthotoluidinotartronates, considered as the primary addition product of an amine upon a keto group, might be expected to lose water readily and give the N=C double bond, which is typical of the usual final reaction product of a substituted amine upon ketone and aldehyde groups $R—N(H)—C(OH) = R_2 \longrightarrow RN = C = R_2 + H_2O$ (oximes, hydrazones, etc.). This we have found to be the case with such derivatives of methyl oxomalonate.[1] In order to obtain the final product, $RN=C=(CO_2C_2H_5)_2$, from these tartronates we have used dehydrating agents to remove the elements of water.

The two toluidinotartronates described above changed but slightly during two months over sulfuric acid, only a few yellow spots appearing. Methyl anilinotartronate soon changes to the yellow iminomalonate under these conditions. These para- and orthotoluidinotartronates were mixed with phosphorus pentoxide in the proportion of one molecule of the former to four of the latter. The mixtures were heated slowly up to 150° during an hour. Although a yellow color was given to the mixture, the product when extracted with ether proved to be chiefly the unchanged tartronates.

Attempts to distil ethyl paratoluidinotartronate with phosphorus pentoxide were made. The substances were mixed, with the latter in excess. After standing three weeks the mixture was dark yellow and sticky. Distillation in a vacuum gave no satisfactory products.

The following experiments yielded better results. 0.4 gram of phosphorus pentoxide (about 3 molecules) was added to 1 gram of ethyl paratoluidinotartronate dissolved in 10 cc. of dry ether. The gummy material above the phosphoric acid residue had a greenish yellow tinge. A thick greenish oil was obtained from the ethereal solution. This could not be made to crystallize. Its properties are similar to those of methyl phenyliminomalonate,[2] $C_6H_5N = C = (CO_2CH_3)_2$. Exposed to

[1] Curtiss and Spencer, THIS JOURNAL, 31, 1057.
[2] *Ibid.*

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the air it absorbs moisture, slowly losing color and the glycerol-like product soon crystallizes in radiating needles. The properties of this substance show it to be the addition product of water on the N=C double bond in $(H_3C)C_6H_4N=C=(CO_2C_2H_5)_2$, regenerating ethyl paratoluidinotartronate. Dry aniline was added to this greenish-yellow oil, much heat was evolved, the color of the oil disappeared immediately and the mass soon crystallized. This also suggests the presence of the N=C double bond. The substance has not been further studied owing to lack of time.

Phosphorus trichloride reacts with ethyl paratoluidinotartronate, as shown by the production of heat and a *yellow* color. After heating the mixture, ether removes a yellow compound which turns white in the air and liberates a gas (HCl?). Its aqueous solution produces an emulsion of paratoluidine when potassium carbonate is added. Phosphorus trichloride has here apparently acted as a dehydrating agent. The resulting ethyl paratoluyliminomalonate $(CH_3)C_6H_4N=C=(CO_2C_2H_5)_2$ is apparently broken up by aqueous alkalies into toluidine and ethyl mesoxalate. This is in perfect analogy with the reaction of water on methyl phenyliminomalonate.[1]

Action of Acetic Anhydride upon Ethyl Paratoluidinotartronate.—1.5 grams of acetic anhydride were slowly added to 3 grams of the tartronate. Reaction takes place with the evolution of heat and the appearance of a deep *yellow* color. The mass solidifies in a short time. Its ethereal solution was shaken in a separatory funnel with a 1 per cent. sodium hydroxide solution, then washed, and dried over calcium chloride, and the ether evaporated. The product was recrystallized from benzene and melted at 150°. Thus prepared it was analyzed.

Calculated for $(CH_3)C_6H_4NH.(CH_3CO_2)$:	C, 59.45:	H, 6.50;	N, 4.34.
Found:	C, 59.66, 59.42;	H, 6.71, 6.82;	N, 4.37, 4.42.

Ethyl acetylparatoluidinotartronate crystallizes in beautiful needles, with satin luster. It is easily soluble in ether, chloroform, carbon disulfide, hot benzene, and hot alcohol, slightly soluble in cold benzene, ligroin, and ethyl alcohol. The acetyl group in this compound may be either upon the oxygen or upon the nitrogen. As this experimental work was done by Mr. Lewis towards the close of the semester some of these products have not been completely studied.

Action of Metatoluidine upon Ethyl Oxomalonate.—0.6 gram of metatoluidine was slowly added to 1 gram of the keto ester (molecular quantities). This caused a rise of about 25° in temperature, loss of color, and the production of a thick honey-like oil. We did not succeed in

[1] To appear in THIS JOURNAL.

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crystallizing this substance nor purifying it by fractional distillation. The analysis was therefore not made.

Benzylamine upon Ethyl Oxomalonate.—Molecular quantities of these substances were mixed at — 13°. Much heat was produced by the reaction and the color quickly changed to a pale yellow. The product was of a glycerol-like consistency, and was turbid, due to the presence of water separated in the reaction. This shows that with this amine the secondary stage in the reaction occurs, in which the elements of water are eliminated. The product could not be distilled and therefore was not analyzed.

Action of Aniline upon Ethyl Oxomalonate.—5.19 grams of aniline in an equal quantity of sodium dry ether were slowly dropped into 9.7 grams of the keto ester (molecular quantities). The mixture was made at —13°. The two liquids reacted intensely with the evolution of much heat. A colorless glycerol-like liquid resulted which crystallized in balls of radiating needles. The product was recrystallized from 50 per cent. alcohol and had a melting point of 117°. The analysis follows:

Calculated for $(C_6H_5NH)_2 = C = (CO_2C_2H_5)_2$: C, 66.62; H, 6.49; N, 8.18.
Found: C, 66.94; H, 6.71: N, 8.08.

This reaction was several times repeated but ethyl dianilinomalonate was the only product separated.[1]

Ethyl dianilinomalonate is a white crystallin compound, easily soluble in chloroform, acetone, carbon tetrachloride, benzene, hot methyl alcohol, and ligroin. It is fairly soluble in cold methyl alcohol, ligroin, and water. This product is identical with that prepared by one of us by the action of aniline on ethyl dihydroxymalonate,[2] and also on ethyl dibromomalonate.[3]

Action of Alcohols upon Ethyl Oxomalonate.—0.26 gram of absolute ethyl alcohol was added at —13° to 1 gram of ethyl oxomalonate (molecular quantities). This caused an elevation of temperature of 50°, a rapid loss of color, and the production of a thick glycerol-like oil. It does not crystallize when cooled to —50°. Attempts at distillation caused a dissociation into the original constituents as indicated in the return of the color of the ketone, and the condensation of alcohol in the upper part of the tube. These reassociate on cooling and the color is again lost. This is in perfect analogy with ethyl dihydroxymalonate where the dissocia-

[1] Mr. Paul S. Burgess, working in this laboratory, has obtained evidence of the existence of the intermediate addition product of aniline upon ethyloxomalonate, $C_6H_5NH.C:(OH) = (CO_2C_2H_5)_2$. It appears to be unstable and a very reactive substance, so much so that after many experiments at low temperature and high dilutions of the reagents, we have been unable as yet to obtain it in a pure form.

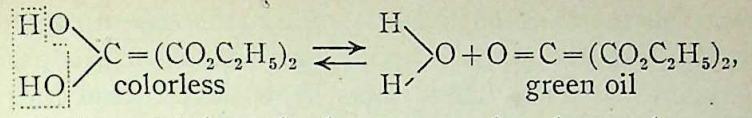
[2] Curtiss, *Am. Chem J.*, 35, 355.

[3] *Ibid.*, 19, 695.

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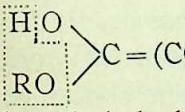
tion into water and the green keto ester takes place around 60°–70°



and reassociation with loss of color occurs a few degrees lower.

Methyl alcohol was mixed in molecular proportions with the ethyl keto ester at —15° and behaved in every way like ethyl alcohol under these conditions. Attempts to purify the thick, colorless syrup by crystallization and distillation failed for the same reasons as mentioned above.

Molecular quantities of benzyl alcohol were likewise mixed at —13° with ethyl oxomalonate. Here also, there was an intense reaction indicated by the evolution of considerable heat and the gradual loss of color of the mixture. The thick oil likewise dissociated when heated into its constituent parts, nor could it be crystallized.

The very characteristic appearance of the reactions, as well as the products, in these keto ester condensations with alcohols leaves no doubt in our minds that these unstable compounds are the primary addition products of the alcohol upon the keto group. $ROH+O=C=(CO_2R)_2 \longrightarrow$ 

They are perfectly analogous to the product formed by ethyl alcohol on methyl oxomalonate. This was obtained first as a colorless glycerol-like syrup, then in the crystallin state, and was readily dissociated, with reappearance of color, into alcohol and methyl oxomalonate when gently heated.[1]

URBANA, ILL.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE STEREOCHEMICAL CONFIGURATIONS OF THE SUGARS FUCOSE AND RHODEOSE.[2]

BY C. S. HUDSON.

Received January 18, 1911.

From the fact that certain varieties of kelp (*Fucus*) yield methylfurfural when distilled with acid, Bieler and Tollens[3] concluded that a methylpentosan is present in these plants. Günther and Tollens[4] hydrolyzed kelp with dilute acid and obtained from it by way of the hydrazone a crystallin sugar which they named *fucose*. Analysis proved it to be a methyl pentose, $CH_3.C_5H_9O_5$, and Laniewsky and Tollens[5] found its

[1] Curtiss and Spencer, THIS JOURNAL, 31, 1055.

[2] Read at the Minneapolis meeting of the American Chemical Society.

[3] *Ber.*, 22, 3062; *Ann.*, 258, 110 (1889); cf. Maquenne, *Compt. rend.*, 109, 603–6 (1889).

[4] *Ber.*, 23, 2585–6 (1890).

[5] *Ber.*, 33, 141 (1900).

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molecular weight by the cryoscopic method to agree with this formula. Müther and Tollens[1] oxidized fucose to the monobasic fuconic acid and lactone and Tollens and Rorive[2] by stronger oxidation produced dibasic *d*-trihydroxyglutaric acid. These facts show that fucose has the constitution $CH_3.CHOH.CHOH.CHOH.CHOH.COH$.

Votocek[3] isolated from the glucoside convolvulin by acid hydrolysis a crystallin methyl pentose and named it *rhodeose* from an older name for convolvulin, *rhodeoretin*. On further study of this sugar Votocek[4] noticed that the melting points of its phenylhydrazone, osazone and other derivatives were practically identical with those of the similar derivatives of Tollens' fucose; and as the sugars themselves have equal and opposit specific rotations (fucose $+75.5°$; rhodeose $-75.5°$), he concluded that they are optical antipodes, similar to *d*-glucose and *l*-glucose. The proof of this interesting and unusual occurrence of antipodal sugars in nature was shadowed by one disagreement, however, for Votocek's rhodeose phenylosazone melted about 20° higher than did the substance which Tollens had described as being fucose phenylosazone. This disagreement was later removed by Votocek[5] who prepared some fucose phenylosazone and found it to melt at the same temperature as did his derivative of rhodeose; about the same time Tollens[6] repeated his work and found that his earlier preparation of fucose phenylosazone contained much hydrazone, and that a new preparation of pure fucose phenylosazone melted at the temperature of Votocek's derivative of rhodeose.

Both Votocek and Tollens have studied the constitution and configuration of these methylpentoses. The former[7] obtained the alcohol, rhodeitol, by reduction of rhodeose with sodium amalgam and found that it is not oxidized by Bertrand's[8] sorbose bacillus. By oxidation of rhodeose with nitric acid he prepared *l*-trihydroxyglutaric acid. From these facts he obtained the configuration of rhodeose by the following reasoning. As *l*-trihydroxyglutaric acid is known to have the configuration

$$\begin{matrix} & OH & OH & H & \\ COOH & . & C & . & C & . & COOH \\ & H & H & OH & \end{matrix}$$

the structure of rhodeitol must be either (*a*)

$$\begin{matrix} & OH & OH & H & \\ CH_3CHOH & . & C & . & C & . & CH_2OH \\ & H & H & OH & \end{matrix}$$

or (*b*)

$$\begin{matrix} & OH & H & H & \\ CH_3CHOHC & . & C & . & C & . & CH_2OH \\ & H & OH & OH & \end{matrix}$$

; and

[1] *Ber.*, 37, 298–308 (1904).
[2] *Ibid.*, 42, 2009–12 (1909); cf. Mayer and Tollens, *Ibid.*, 40, 2434–40 (1907).
[3] *Z. Zuckerind. Böh.*, 24, 248–57.
[4] *Ibid.*, 25, 297–305; 27, 15–27.
[5] *Ber.*, 37, 3859–62 (1904).
[6] Mayer and Tollens, *Ibid.*, 38, 3021–2 (1905)
[7] *Ibid.*, 43, 469–75 (1910).
[8] *Ann. chim. phys.*, [8] 3, 181.

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that of rhodeose must be either (I) $CH_3.CHOHC \overset{OH\ OH\ H}{.\ C\ .\ C.COH}$ or (II) $CH_3.CHOH.C \overset{OH\ H\ H}{.\ C\ .\ C.COH}$. Bertrand's sorbose bacillus has been found to oxidize only those alcohols in the structure of which the two carbon atoms nearest the CH_2OH group have similarly placed hydrogen atoms. As Votocek could detect no action of the bacillus on rhodeitol, he concluded that the latter cannot have the structure (*b*) and must therefore have (*a*). From this structure of rhodeitol (*a*) that of rhodeose (I) follows directly. The proof is interesting and suggestive, but most chemists will doubtless agree that in so far as it depends upon the non-action of the bacillus it is not as convincing as could be wished.

Tollens and his students, Mayer and Rorive,[1] have presented independent evidence on the constitution of fucose. Starting from the fact that the sugar yields *d*-trihydroxyglutaric acid by oxidation with nitric acid, it must be concluded that its constitution is limited to the antipodes of (I) and (II). A choice between these configurations was made by Tollens from the results of a study of the fucohexonic acids which result from fucose by the cyanide synthesis. If the antipode of (I) applies to fucose the two possible fucohexonic acids have the respective constitutions $CH_3.CHOHC \overset{H\ H\ OH\ OH}{.\ C\ .\ C.COOH}$ and $CH_2.CHOH.C \overset{H\ H\ OH\ H}{.\ C\ .\ C.COOH}$, $\qquad\qquad\qquad

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tion (I) applies to fucose. Votocek[1] has supplied the other side of the evidence by isolating, though in an impure condition, the acid potassium salt of saccharic acid from the oxidation products of the rhodeohexonic acids which result from rhodeose by the cyanide synthesis. He was unable to detect any mucic acid in these products and therefore concluded from a course of reasoning similar to that of Mayer and Tollens that rhodeose has configuration (I) and fucose the antipodal structure.

The purpose of this article is to show that the configuration of rhodeose and fucose can be obtained by a third, independent method which is based upon a recently found relation between the constitution and the optical rotatory power of the sugar lactones.[2] The description of the extensive evidence upon which this method is based will be found in detail in the former article. It may suffice to recall the principle upon which the method depends, namely, that the "lactones of dextrorotation have the lactonic ring on one side of the structure (in the customary symbols, the lower side), lactones of levorotation have it on the other, and the position of the ring shows the former position of the OH group on the γ-carbon atom." Writing the carbon chain of rhodeose $CH_3.CHOH.C\ .\ C\ .\ C.COH$ (1) (2) (3) and referring to the fact that the rotation of rhodeonic lactone is $-76°$[3] it will be seen that the lactonic ring from the end carbon to its γ-carbon is above the carbon chain and consequently the hydrogen atom in the sugar is below atom (1). The rotations of the rhodeohexonic lactones were found by Krauz[4] to be $-35°$ and $-41°$, or in other words decidedly negative for both substances; consequently by similar reasoning the hydrogen atom in the sugar is to be chosen below carbon (2). The structure of rhodeose

OH OH |

is thus determined partially to be (III) $CH_3.CHOH.C\ .\ C\ .\ C.COH.$

H H |

If the specific rotation of the heptonic lactones from fucose or rhodeose were known, the configuration of the groups attached to carbon (3) could be decided. In the absence of these values another way must be followed. From the fact that rhodeose yields *l*-trihydroxyglutaric acid on oxidation its structure must be either I or II (see preceding), and as only structure I has the hydrogen atoms below carbons (2) and (3), as required by III, it must be selected for rhodeose. The structure of fucose is then the mirror image of I.

It will be noticed that a configuration of the group $CH_3.CHOH$, which

[1] *Ber.*, 43, 474 (1910).

[2] THIS JOURNAL, 31, 338–46 (1910).

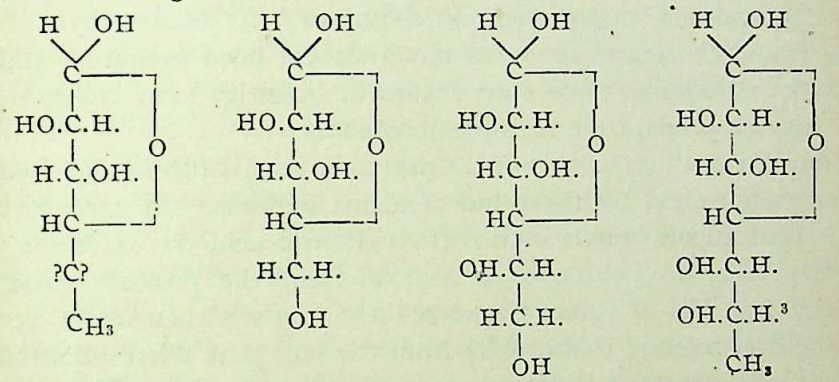
[3] Votocek, *Z. Zuckerind. Böh.*, 25, 297 (1902). Müther and Tollens (*loc. cit.*) found the specific rotation of fuconic lactone to be $+71°$ to $+78°$, which agrees with the accepted antipodal relation between fucose and rhodeose.

[4] *Ber.*, 43, 486 (1910).

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is an asymmetric one, is not indicated in I. The reason for this omission is that none of the facts which have been adduced to prove the structure of the other asymmetric groups has any bearing on the configuration of this one. Lately Tollens[1] has expressed the view that this group has the same structure in fucose that it has in *l*-galactose for the reason that the two sugars have nearly the same rotations, —75.5° and —81°. Votocek[2] does not consider this evidence of any weight. Regarding this question the following may be presented. The four sugars, fucose, *d*-arabinose, *l*-galactose and *l*-α-rhamnohexose have a large portion of their structure in common, as will be seen from the formulas, which are here printed in the γ-lactonic ring form.



Fucose. *d*-Arabinose. *l*-Galactose. *l*-α-Rhamnohexose.

The portions of the structures included by the lactonic rings are identical, but the portions below vary greatly, being in one case (*d*-arabinose) not even asymmetric. The specific rotations[4] of these sugars, or more correctly of the stable solutions which contain their α and β-forms in equilibrium, are, fucose —75.5°, *d*-arabinose —105°, *l*-galactose —81° and *l*-α-rhamnohexose —61°. These values are sufficiently alike, especially when they are reduced to the molecular rotations, to show that the common structure included within the lactonic rings is the principal factor in fixing the rotation, and that the latter depends only in a minor degree upon the groups below the rings. This conclusion is emphasized by a peculiar relation between the rotations of these sugars and those of their lactones. Fuconic lactone rotates +75°, *d*-arabonic +74°, *l*-galactonic +78°, *l*-α-rhamnohexonic +84°,[5] or in other words the lactones have almost identical rotations, which are of opposit sign from those of the sugars. This evidence shows again that the rotations

[1] *Ber.*, 40, 2438 (1907); 42, 2012 (1909).

[2] *Ibid.*, 43, 469–75 (1910).

[3] The configuration of this group follows from the structure of rhamnose. See THIS JOURNAL, 31, 345 (1910).

[4] Quoted from Lippmann's "*Chemie der Zuckerarten.*"

[5] For references see THIS JOURNAL, 31, 338–46 (1910).

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of these sugars and their lactones are principally due to their common element of structure which is within the lactonic ring, and that the configuration, weight, etc., of the groups which they do not possess in common have only a minor influence on the rotatory powers. Since such is the case it is hardly possible to agree with Tollens that the configuration of any of the groups below the ring can be decided from the rotations of the sugars. The only way at present known by which the configuration of the doubtful CH_3.CHOH group of fucose and rhodeose can be determined is from a knowledge of the sign of the rotation of the methyl tetronic lactones which should be yielded by these sugars. This method has been used in determining the configuration of the similar group in the related methyl pentose, rhamnose,[1] but the methyl tetronic lactones from fucose and rhodeose have not yet been prepared, and the difficulty of obtaining these rare sugars in quantity prevents me from attempting the preparation of these substances.

To summarize, the structure of the antipodal sugars fucose and rhodeose has been determined by three independent methods. In each of these the fact that fucose yields *d*-trihydroxyglutaric acid on oxidation, and rhodeose, *l*-trihydroxyglutaric, is used to limit the possible structures to forms I and II. A choice between these forms is then made, according to the first method (Votocek's) from the fact that Bertrand's sorbose bacillus does not attack rhodeitol, according to the second (Tollens' and Votocek's) from the fact that the oxidation of fucohexonic and rhodeohexonic acids does not yield crystallin mucic acid, and according to the third method, from the fact that rhodeonic and rhodeohexonic lactones are of strong negative rotations. The three methods give the same conclusion, namely, that rhodeose has the structure I and fucose the antipodal configuration. The configuration of the first asymmetric group of these sugars CH_3.CHOH remains entirely undetermined, but could doubtless be decided from a knowledge of the rotatory powers of the methyl tetronic lactones from fucose and rhodeose, which however have not yet been prepared on account of the difficulty of obtaining the sugars.

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE DIVISION OF CHEMISTRY, HYGIENIC LABORATORY, U. S. PUBLIC HEALTH AND MARINE HOSPITAL SERVICE.]

LUCIFERESCEINE,[2] THE FLUORESCENT MATERIAL PRESENT IN CERTAIN LUMINOUS INSECTS.

BY F. ALEX. MCDERMOTT.

Received January 16, 1911.

In 1909, Dr. W. W. Coblentz,[3] of the U. S. Bureau of Standards, an-

[1] THIS JOURNAL, 31, 348.

[2] In my own notes I have adopted this name as representing the fluorescent

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nounced that during the course of his work with Dr. Ives on the luminous efficiency of the firefly, *Photinus pyralis*,[4] he had discovered that this insect contains a substance whose solutions possess a bright blue fluorescence, and that the spectrum of the fluorescent light of such solutions is complementary to that of the emitted light of the insect. At this time I was engaged with Professor Joseph H. Kastle, of the University of Virginia (then Chief of the Division of Chemistry of the Hygienic Laboratory), in a study of the effects of various chemical reagents on the luminous tissue of the firefly,[5] and after some correspondence with Dr. Coblentz, took up a study of the chemical behavior of this fluorescent substance, with the view of determining its nature. As yet the work is by no means complete, owing partly to the lack of sufficient material, and hence the following paper will present only certain qualitative results which have been obtained on the small amount so far available; it is hoped to secure a larger quantity of the fluorescent material during the coming summer, and extend the inquiry.

Since its original discovery by Dr. Coblentz in *Photinus pyralis*, it has been found by him in *Photinus corruscus* and in *Photuris pennsylvanica*, all species of Lampyridae. I have been unable to verify the presence of this substance in *Photuris pennsylvanica*, but have, in addition, found it in *Photinus scintillans*. All of these insects possess a strong, rather rank, characteristic odor, and the Photinini exude, when irritated, a sticky, milky fluid, which hardens in the air; in this secretion the fluorescent material is largely present. These insects, and especially their larvae, are carnivorous, feeding on snails, earth-worms, etc.

In addition to the Lampyridae above noted, Dubois[6] records that there is present in the juices of the cucuyo, the large Cuban elaterid firefly, *Pyrophorus noctiluca*, a substance whose solutions show a blue fluorescence. Dubois considered this substance to be essential to the photo-

substance derived from the firefly, the first three syllables agreeing with Dubois' "Luciferine" and "Luciferase" and the last three being merely the termination of "fluorescein" with "*e*" added to make the termination representing an alkaloid. Whether the formation of the name is justified by the constitution of the substance remains to be seen; I have no intention of encumbering the nomenclature of organic chemistry with a new variation.

Right here I might say that there is an unfortunate confusion in the minds of many people between "fluorescent" and "phosphorescent" materials, especially when mentioned in connection with the firefly, and that the substance which forms the basis of this paper is not the substance which produces the light of the Lampyridae and other photogenic insects.

[3] Coblentz, *Physik. Z.*, 10, 955–6 (1909). See also Ives and Coblentz, 2.

[4] Ives and Coblentz, *Bulletin of the Bureau of Standards*, Washington, 6, 321–36 (1910).

[5] Kastle and McDermott, *Am. J. Physiol.*, 27, 122–51 (1910).

[6] Dubois, *Bull. soc. entomologique de France*, 11, 1–275 (1886).

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genic process of the insect, and ascribed to the actinic power of the blue rays in its fluorescent light, the actinic power of the emitted light of the insect. The substance itself he considered as analogous to esculin, indeed his work might be taken to indicate that he considered it to be esculin.[1] Dubois observed that the substance he extracted from the cucuyo acquired its maximum intensity of fluorescence at wave length 0.391μ in the ultraviolet. Without developing this line further, it will suffice to say that the fluorescent solutions derived from the material present in the Lampyridae, fail to give any of the reactions for esculin given in Watts' Dictionary, or any that I have found elsewhere. The cucuyo belongs to a group of beetles entirely unlike the Lampyridae, and known as the Elateridae; it is herbivorous, living largely on sugar cane. In view of these differences there may be some reasonable doubt as to whether the substances found in the two groups of insects are identical; I have had no opportunity to test this point. It is nevertheless remarkable that two insects as widely separated in classification as *Pyrophorus noctiluca* and *Photinus pyralis*, and having nothing else in common except the possession of the photogenic function, should both yield substances whose solutions show a blue fluorescence.

I have extracted the margined soldier beetle (*Chauliognathus marginatus*), a near relative of the Lampyridae and formerly classed with them, but which is diurnal and non-luminous, and obtained an extract containing a yellow dye, and non-fluorescent. Extracts of the local species of cantharid (*Epicauta pennsylvanica*) also yielded yellow dyes, but no fluorescence; and a single species of carabid (*Chlaenius sericeus*), which has a strong, characteristic odor, failed to give either a dye or fluorescence. In all these cases, alcohol was used as the extractant. In a private communication, Mr. T. Davidson Arndt, of Trinidad, B. W. I., states that he has observed independently "the production by most insects of substances which under the X-rays are strongly fluorescent."

Fluorescent substances are by no means uncommon, and in spite of the great amount of work that has been done upon it, it is pretty difficult to ascribe to any special group or arrangement the production of fluorescence. Fluorescent substances of various natures are not infrequent among lower animals (see von Fürth),[2] and the fluorescent pigments known as lipochromes occur in many Coleoptera. Luciferesceine, however, appears to offer objections to including it in any of the classes of fluorescent materials so far found in animal organisms. Of the insects named as containing luciferesceine, all are luminous and nocturnal in

[1] Esculin (aesculin) is a glucoside found in the horse chestnut, which on hydrolysis yields glucose and esculetin (dihydroxycoumarin). In alkaline alcoholic and aqueous solutions it shows a strong blue fluorescence.

[2] von Fürth, *Vergleichende chemische Physiologie der niederen Tiere*, Jena, 1903, 551–60.

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habit, except *Photinus corruscus*; this species, although a true lampyrid, has become diurnal in habit, and has lost its luminous function, except, it is said, while in the larval stage. Lampyrids as a class are rejected as inedible by most insectivorous creatures; toads and frogs present perhaps the only exception to this rule, and in view of the well-known wide scope of the gastronomic attainments of these animals, this can scarcely be taken as a fair criterion of the edibility of Lampyridae for most other insectivorous creatures. Children in this locality (Washington, D. C.) seem to quite generally regard the fireflies as poisonous, but this view appears to be by no means universal. In some localities, the larvae of the cucuyo are said to be used as food.

To obtain this substance for study, Dr. Coblentz extracted the insects with ether, added water to the extract, precipitated the proteins with lead acetate, and concentrated by boiling. The material I have used has for the most part been obtained in either of two ways: The first of these was to extract the entire insects (in the early stages of the work the luminous segments had been removed for other work) with absolute alcohol in a Soxhlet extractor; the extract is yellow, and becomes brownish orange on concentration. It is impossible to bring this extract to dryness on the water bath or in a vacuum desiccator. A thick, dark syrup is left, which decomposes if heated to a temperature materially higher than 100°. For the purpose of removing as much of the foreign matters as possible, the alcoholic extract was treated with lead acetate solution and allowed to stand 24 hours, filtered, and the precipitate washed with absolute alcohol, crystallin ammonium sulfate added and the solution allowed to stand for another 24 hours, and then decanted through a filter. The resulting solution is yellow, with a strong blue fluorescence, and on evaporation yields a brownish syrup from which the excess of ammonium sulfate crystallizes out. On taking up again with absolute alcohol the excess of sulfate remains, and the fluorescent substance goes into fairly pure solution. Some other organic compounds are, however, undoubtedly present. The second method of obtaining the luciferesceine was to wash out the tubes, bottles, etc., in which the insects had been collected, with absolute alcohol, preferably allowing it to stand for several hours in them. In these tubes the sticky secretion before referred to may be seen hardened in specks all over their inside surfaces, and from this secretion the alcohol dissolves out the luciferesceine. Such solutions, after filtration, are clear and colorless, and show a strong blue fluorescence. The solution may be evaporated to dryness, and leaves a white or slightly yellow, solid, non-crystallin material, apparently the fluorescent material in the purest form in which it has yet been obtained. So far all attempts to secure the luciferesceine in crystallin condition have ailed, but that obtained by the evaporation of the alcoholic extract of

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the deposited secretion of the insects acts in such a way as to lead me to believe that it is very nearly a single substance, even if not quite pure. Heat, up to the boiling point of water, does not appear to affect the stability of luciferesceine; at higher temperaures it melts and boils, giving off an unpleasant, fishy odor, chars with the evolution of an inflammable gas, and finally leaves a very slight ash. Under ordinary conditions of temperature and humidity, the luciferesceine seems to be very stable. Insects collected in Massachusetts over thirteen years ago, and preserved dry, pinned in a cabinet ever since, yielded fluorescent extracts with alcohol.

In the alcoholic extract of the whole insects, after purification, chloroplatinic acid produces a yellow precipitate which appears to be a mixture of the chloroplatinates of potassium and lecithin. The filtrate from these chloroplatinates, containing an excess of platinum, may be rendered alkaline, the platinum precipitated by hydrogen sulfide in large excess, and the platinum sulfide filtered off, and a clear, slightly yellow, fluorescent solution obtained, which still contains other organic matters. As long as hydrochloric acid is present, the solution does not show its fluorescence. In this extract of the whole insect, silver nitrate solution produces a white precipitate, which rapidly turns brown; mercuric chloride produces a white precipitate; ferric chloride gives a brown precipitate. Examined in a layer 15 mm. thick, the moderately concentrated solution shows a shortening of the violet end of the solar spectrum. The extract leaves a greasy feeling on evaporation on the fingers. On standing exposed to the light, the fluorescence gradually weakens, and a light brown precipitate is formed. The precipitate dissolves in aqueous alkali, forming a brownish, non-fluorescent solution.

With the extract derived from the deposited secretion, and which I regard as being fairly pure, chloroplatinic acid produces no precipitate. Lead acetate produces no immediate precipitate, but after boiling and standing, a very slight, white precipitate is formed (this may, of course, be a basic lead compound); the supernatant fluid is fluorescent. Mercuric chloride produces a slight cloudiness at first; after boiling and standing, a slight yellow precipitate is formed; supernatant fluid not fluorescent. Silver nitrate produces no immediate precipitate; after boiling and standing, a slight brown precipitate is formed. The supernatant fluid is not fluorescent. Magnesia mixture produces a white, flaky precipitate, but the supernatant fluid retains its fluorescence. Ammonium molybdate produces a faint opalescence, but does not destroy the fluorescence. Uranium nitrate produces no precipitate, but its yellow color masks the fluorescence; the same is true of ferric chloride, potassium dichromate, picric acid, and iodine. One per cent. osmic acid causes a faint opalescence, which darkens on heating. Ammonium sulfate produces no pre-

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cipitate. Potassium ferrocyanide produces in some solutions a dense, cream-colored precipitate, and the supernatant fluid is no longer fluorescent. I have not as yet had an opportunity to study this precipitate. Three per cent. phosphotungstic acid produces only a slight opalescence, but 3 per cent. phosphomolybdic acid produces in some solutions a cream-colored precipitate, and what appear to be drops of oil adhere to the sides of the test tube; these, however, fail to dissolve in ether. Alkaline cupric sulfate solution produces a white precipitate.

The luciferesceine remaining on the evaporation of the extract from the secretion dissolves best, and with the production of fluorescent solutions, in water, ethyl alcohol, amyl alcohol, and glycol; it is less easily soluble in ether, and the solution shows a weaker fluorescence. It does not appear to be soluble in carbon tetrachloride, benzene, acetone, or chloroform; it dissolves to some extent in pyridine, and the resulting solution is slightly fluorescent. With glycerol it appears to react slowly, forming a yellow solution, and with concentrated sulfuric acid it reacts energetically, with charring, and reddening of the acid. It does not give the murexide test.

The injection into mice of weak solutions in physiologic salt solution produced no noticeable immediate results, although after twelve hours the animal was evidently somewhat sleepy, and showed slow respiration. In larger doses it acts first as an irritant; later the animal shows drowsiness, and sometimes slow respiration. Dr. W. H. Schultz, who was good enough to make these injections for me, suggests that these effects might be due to a trace of cantharidine, which is present in many Coleoptera.

The urates and phosphates of sodium, potassium, ammonium and calcium have been found in the tissue and ash of the luminous organs of the Lampyridae and Elateridae, and the inner layer of the photogenic organs of these insects is said to consist of guanine, and sodium or ammonium urate.

Most of the substances yielding fluorescent solutions, which have been found in the tissue of lower organisms, have been lipochromes or other pigments. The fact that luciferesceine is not a colored substance and that it does not dissolve in the usual fat solvents—benzene and carbon tetrachloride—are sufficient to render the view that it might be a lipochrome untenable. Its conduct with various precipitants, its solution with a reddish color in sulfuric acid, and its chemical conduct in general have led me to regard it as alkaloidal in nature. That it is not a necessary factor in biophotogenesis is evidenced by its existence in non-luminous species. It cannot be a fluorescent chlorophyll derivative since it is found in carnivorous insects.

By the researches of Tappeiner and others, it has been shown that

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fluorescent materials in the organism affect the activity of diastase and other enzymes. In the instance of luciferesceine, we have a strongly fluorescent material normally present in considerable amounts in an organism; it can here evidently exert no deleterious action upon the organism containing it. Most, but not all of the organisms containing it, however, are nocturnal in habit, and their activities depressed by exposure to light. It is of interest to note in this connection, that according to the theory of fluorescence as a "step-down" process of radiation, and the law of Stokes expressing this theory, luciferesceine should fail to show fluorescence in the emitted light of the insect, since all of the light emitted by the insect is less refrangible than the longest wave length in the fluorescent light of luciferesceine; however, Nichols and Merritt[1] have shown that Stokes' law fails to hold good for many common fluorescent substances, and my own experiments indicate that any light within the visible spectrum of shorter wave length than the yellow-orange, will excite a visible fluorescence in solutions of luciferesceine. On the whole it seems that this substance is contained in a defensive secretion of the insect, and that its fluorescence is a property dependent on its chemical constitution and having no reference to the life processes of the organism or possibly to its defensive function either.[2]

In conclusion I wish to express my indebtedness to Dr. Wm. W. Coblentz, of the Bureau of Standards, the original discoverer of luciferesceine in the Lampyridae, to Dr. Carl L. Alsberg, of the Bureau of Plant Industry, and to Dr. W. H. Schultz and other workers in the Hygienic Laboratory, for assistance and advice in this work, and to Dr. E. A. Schwarz and Mr. H. S. Barber, of the U. S. National Museum, for entomologic information.

THE PREPARATION AND PROPERTIES OF AN OXIDASE OCCURRING IN FRUITS.

By H. P. Bassett and Firman Thompson.

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Within recent years there have been numerous reports on the existence of a class of enzymes which are capable of promoting various oxidizing processes, and which appear to be very widely distributed in both plants and animals. To this class of enzymes the generic name of oxidases has been given.

[1] Nichols and Merritt, *Physic. Rev.*, 16, 18–36 (1904).

[2] Jordan (*Botanical Gaz.*, Chicago, 27 (1899)) arrived at a somewhat similar conclusion in regard to the fluorescent pigment of *Bacillus fluorescens liquefaciens*. Although this pigment is yellow, with a green fluorescence, it shows some analogies to luciferesceine; it is soluble in water, but not in carbon tetrachloride, chloroform, ethyl alcohol or ether, and does not appear to be precipitated by lead acetate or ammonium sulfate.

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Among the first of these enzymes to be discovered was laccase, occurring in the sap of the lac tree, by Yoshida.[1] Some years later Yoshida's results were confirmed by Bertrand,[2] who also showed that it was able to oxidize certain aromatic compounds which contain at least two NH_2 or OH groups, *e. g.*, hydroquinone to quinone, pyrogallol to purpurogallin, etc. He has also reported its occurrence in many other plants of widely different families.

Martinand[3] reports the presence of a similar, if not identical, enzyme called oenoxydase in ripe grapes, and which is probably the cause of a peculiar disorder of wines known as "la casse."

Lindet[4] has also investigated a similar enzyme occurring in the juice of the apple, which causes the oxidation of various aromatic compounds, among others that of pyrogallol to purpurogallin.

In carrying out some analyses of fruits in connection with the Department of Plant Pathology of the Delaware Experiment Station, it was noted by one of the writers that the tannin, as determined by Carpene's ammoniacal zinc acetate method, showed widely divergent results on samples of the same fruits taken at the same time but under slightly different conditions. While the method is not all that could be desired for this determination, it was shown by the analysis of solutions of known tannin content, that the discrepancies could not be entirely attributed to deficiencies of the method.

The results seemed to show a marked and rapid increase of tannin on injury of any kind which allowed access of air. For instance, a sample was taken by dropping the fruit into boiling water immediately after plucking and the tannin determined at once. At the same time another sample of fruit on the same tree was injured by repeated puncturing of the stem and fruit with a pin and allowed to remain on the tree for 48 hours, when the tannin was determined. The tannin in the injured fruit was about three times that of the uninjured. In another case apples that had fallen from the tree showed about twice as much tannin as those freshly plucked.

From these and other similar results the conclusion was drawn that tannin or a tannin-like substance (since this method probably includes compounds other than true tannic acid) was formed comparatively rapidly on exposure of the injured fruit or fruit pulp to the air. It was thought if this were the case that it would probably be shown by a decrease in the soluble nitrogen of the juice due to the precipitation of the soluble proteins by the tannin formed. Accordingly, juices were pre-

[1] *J. Chem. Soc.*, 43, 472.
[2] *Compt. rend.*, 118, 1215.
[3] *Ibid.*, 121, 512.
[4] *Ibid.*, 120, 370.

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pared from a number of different fruits by first grinding through an ordinary meat chopper and pressing through fine Canton flannel. The materials used were green walnut hulls, ripe apples, green apples and pears.

The juices were sampled immediately after pressing out and every 24 hours thereafter, the samples being filtered through asbestos, using suction. In the case of the walnut hulls the juice was divided into two portions, one of which was raised to boiling temperature and kept there for thirty minutes. The results in the following table are expressed as grams of soluble nitrogen in 50 cc. samples of the juice.

	Fresh juice.	22 hours.	46 hours.	94 hours.
Walnut hulls, natural	0.2646	0.2372	0.2365	0.2219
Walnut hulls, boiled	0.2646	0.2604	0.2632	0.2478
Ripe apples	0.0074	0.0072	0.0074	..
Green apples	0.0106	0.0076	0.0038	..
Pears	0.0151	0.0105	0.0130	..

The sampling was discontinued in each case when fermentation was apparent. It will be noted that while the boiled walnut juice showed practically no decrease in soluble nitrogen the unboiled juice showed a gradual decrease amounting to 16 per cent. in 94 hours. Unripe apples showed the greatest decrease, amounting to 64 per cent. in 46 hours.

This series of experiments would seem to indicate that there was a compound formed, which was probably of the nature of a tannin, having the power to convert the nitrogen into an insoluble form.

A similar series of experiments was then arranged in which the fruits were ground with calcium carbonate as suggested by Appleman's work on catalase.[1] The results are given in the following table expressed as grams of nitrogen in 50 cc. as before.

	Fresh juice.	24 hours.	48 hours.	72 hours.
Walnut hulls, natural	0.2202	0.2666	0.2565	0.2311
Ripe apples	0.0034	0.0021	0.0021	..
Green apples	0.0083	0.0084	..	..
Pears	0.0113	0.0130	..	..

As before the sampling was discontinued when fermentation was plainly evident. It will be noted that there was practically no change in the soluble nitrogen in the time covered by the experiments. There is at present no adequate explanation of the increase in soluble nitrogen shown by the walnut juice during the first 48 hours. Fermentation was apparent in about thirty-six hours after preparation, which was a considerably shorter time than in the previous experiments.

From these results it was concluded that there was an oxidizing enzyme present which was only active in acid solutions and which has been prepared in the following manner from pears.

[1] *Botan. Gaz.*, 50, 182.

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The fruit is ground with calcium carbonate in an ordinary meat chopper and the juice expressed through Canton flannel and allowed to settle in a cool place over night. The supernatant liquid is then drawn off the top and somewhat more than an equal volume of 95 per cent. alcohol added to it. The precipitate which is produced is then allowed to settle, the supernatant liquid siphoned off and the precipitate collected on a Buchner funnel. This precipitate contains the enzyme and may be prepared for use by suspension in water.

It having been found by Bertrand in working with laccase and by Lindet with an oxidase found in cider and wines that these enzymes possessed the property of oxidizing certain polyatomic phenols, *e. g.*, hydroquinone to quinone and pyrogallol to purpurogallin, an attempt was made to study the properties of the enzyme by preparing artificial solutions of gallic acid and albumin and measuring the rate and extent of formation of any tannin-like compounds by the decrease of the soluble nitrogen. The following series of solutions were accordingly prepared.

No. 1. 200 cc. 1 per cent. gallic acid solution and 300 cc. water.
No. 2. 200 cc. 1 per cent. gallic acid solution, 100 cc. albumin solution, 200 cc. water.
No. 3. 200 cc. 1 per cent. gallic acid solution, 50 cc. enzyme suspension, 250 cc. water.
No. 4. 200 cc. 1 per cent. gallic acid solution, 100 cc. albumin solution, 50 cc. enzyme suspension and 150 cc. water.
No. 5. 50 cc. enzyme suspension, 100 cc. albumin solution and 350 cc. water.
No. 6. 50 cc. enzyme suspension, and 450 cc. water.
No. 7. Same as No. 1 with addition of 50 cc. of 3 per cent. hydrogen peroxide.
No. 8. Same as No. 2 with addition of 50 cc. of 3 per cent. hydrogen peroxide.
No. 9. Same as No. 3 with addition of 50 cc. of 3 per cent. hydrogen peroxide.
No. 10. Same as No. 4 with addition of 50 cc. of 3 per cent. hydrogen peroxide.
No. 11. Same as No. 5 with addition of 50 cc. of 3 per cent. hydrogen peroxide.
No. 12. Same as No. 6 with addition of 50 cc. of 3 per cent. hydrogen peroxide.

The albumin used was a solution of egg white in water and contained 1.36 grams of nitrogen per liter. The enzyme suspension was prepared in the manner indicated above, 50 cc. containing 0.00448 gram nitrogen.

In about an hour after the addition of the enzyme, a very heavy, flocculent precipitate had formed and settled in the flasks containing all three constituents, *viz.*, gallic acid, albumin and enzyme. Those containing gallic acid and enzyme without albumin had turned a rich wine-red color, presumably from the oxidation of the gallic acid.

Samples of 50 cc. each were taken after 15 hours and every 24 hours thereafter until there was no longer any decrease in the nitrogen or until the solution showed signs of fermentation. The results in the following table are expressed as grams of soluble nitrogen in 50 cc.

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No.	Nitrogen present.	15 hours.	39 hours.	63 hours.	87 hours.	137 hours.	161 hours.
1	0.0013	0.0016	0.0013	..	..	..	..
2	0.0149	0.0146	0.0146	0.0143	0.0147	0.0146	..
3	0.0017	0.0018	0.0017	..	..	..	..
4	0.0153	0.0113	0.0106	0.0102	0.0077	0.0044	0.0032
5	0.0140	0.0138	0.0146	..	..	..	..
6	0.0004	0.0013	0.0010	..	..	..	..
7	0.0013	0.0018	0.0018	..	..	..	..
8	0.0149	0.0153	0.0145	0.0149	0.0151	..	..
9	0.0017	0.0017	0.0017	..	..	..	..
10	0.0153	0.0081	0.0048	0.0037	0.0035	..	..
11	0.0140	0.0147	0.0149	..	..	..	..
12	0.0004	0.0020	0.0014	..	..	..	..

Three days after the experiment had been started, tannin determinations were made by precipitation with hide powder, titrating before and after the precipitation with tenth-normal permanganate. In the following table the results are expressed as the number of cc. of tenth-normal permanganate required by 10 cc. of the liquid.

No.	Before precipitation.	After precipitation.	Difference.	No.	Before precipitation.	After precipitation.	Difference.
1	15.1	15.2	—0.1	7	28.5	24.3	4.2
2	18.0	17.8	0.2	8	29.1	27.0	2.1
3	18.0	15.0	3.0	9	30.5	27.7	2.8
4	18.1	16.3	1.8	10	31.5	28.6	2.9
5	5.8	6.0	—0.2	11	13.5	11.5	2.0
6	5.6	5.8	—0.2	12	13.3	13.4	—0.1

The differences in titration, which would represent the tannin precipitated by the hide powder are insignificant except in the cases where the enzyme and gallic acid were present together in the series containing no hydrogen peroxide. Where hydrogen peroxide was present there would appear to have been some oxidation due to it alone, as important differences were shown in almost every case.

Each of these solutions was also tested for tannin by Oliver's ammonia-nitric acid test as given in Cohen's "Tests and Reagents" with the following results:

No. 1. No precipitate
No. 2. No precipitate
No. 3. Heavy precipitate
No. 4. Heavy precipitate
No. 5. No precipitate
No. 6. No precipitate
No. 7. No precipitate
No. 8. No precipitate
No. 9. No precipitate
No. 10. No precipitate

Since it had been previously observed that the juices that had been prepared by grinding with calcium carbonate and in which there was apparently no action of the enzyme, fermented much sooner than the juices that had been prepared by grinding without calcium carbonate, it was thought that the substances formed in the reaction might have

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some germicidal properties. Accordingly, six days after the gallic acid series of experiments had been started, cultures on agar-agar, gelatin and beef tea were made from the solutions Nos. 2, 3, 4 and 5.

Ninety-six hours after the setting of the cultures the following results were noted:

No.	Agar-agar.	Gelatin.	Beef tea.
2	Heavy fungus growth	Heavy fungus growth	Cloudy
3	One colony	One colony	Clear
4	Slight growth	liquefied	Slight cloudiness
5	Heavy growth	liquefied	Cloudy

In both cases where the gallic acid and enzyme were not present together there was a heavy fungus growth and in both cases where they were present there was only a very slight growth in any of the media.

The conclusion would seem to be justified that the substance formed by the action of the enzyme and gallic acid shows a marked inhibitive effect on fungus and bacterial growths.

From the almost instantaneous appearance of the precipitate and from the figures obtained for soluble nitrogen it was inferred that the action was comparatively rapid and accordingly an experiment was planned to test this point.

A solution consisting of 100 cc. of albumin solution containing 1.52 grams of nitrogen per liter, 200 cc. of 1 per cent. gallic acid solution, 50 cc. of enzyme suspension and 50 cc. of 3 per cent. hydrogen peroxide was diluted to 500 cc. Another solution which was the same in every respect with the exception of the hydrogen peroxide, which was omitted, was prepared at the same time. Samples of these two solutions were taken every fifteen minutes for about two hours and the soluble nitrogen determined.

The solutions could not be obtained clear on filtering and no flocculent precipitate separated out as in the previous series.

The determinations of nitrogen are given in the following table, the figures representing the number of grams of nitrogen in 50 cc. as before.

	N present.	15 min.	45 min.	75 min.	105 min	165 min.
With H_2O_2.....	0.0152	0.0158	0.0144	0.0147	0.0147	0.0143
Without H_2O_2....	0.0152	0.0151	0.0141	0.0154	0.0148	0.0127

As will be noted there was very little, if any, action taking place in this series of experiments and accordingly 60 cc. more of the enzyme suspension was added in each case. Immediately a flocculent precipitate formed, which settled very rapidly. Samples taken ten minutes after the addition of the enzyme and filtered as rapidly as possible showed the following amounts of soluble nitrogen in 50 cc.

With H_2O_2.....	0.0090
Without H_2O_2....	0.0076

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The same experiment was then repeated with the constituents in the same proportion as before except the quantity of the enzyme suspension which was increased to 150 cc. Samples were taken every fifteen minutes for the first hour and at longer intervals thereafter up to four and one-half hours. The determinations of soluble nitrogen are given in the following table:

	15 min.	30 min.	45 min.	1 hour.	1½ hrs.	2 hours	4½ hrs.
With H_2O_2....	0.0112	0.0119	0.0120	0.0120	0.0125	0.0115	0.0109
Without H_2O_2	0.0122	0.0123	0.0123	0.0123	0.0122	0.0116	0.0123

The nitrogen present at the beginning of the experiment was 0.0159 gram in each case. It will be noted that in the first case there was a decrease in soluble nitrogen amounting to about 30 per cent. and about 23 per cent. in the second with practically no further change up to four and one-half hours, when sampling was discontinued. From these results it was concluded that the action of the enzyme was very rapid and that it takes place only when the concentration is above a certain minimum.

The enzyme as prepared in the manner previously indicated deteriorates rapidly in slightly acid solutions and can not be dried. It can be preserved for a considerable time on ice, in chloroform water and in 5 per cent. alcohol. It produces an intense blue color with an alcoholic solution of guaiacum when one or two drops of acetic acid are added to the solution. A neutral solution gives a dirty green precipitate.

The freshly prepared juice also produced this blue color when it was slightly acid.

By this means an attempt was made to study the localization of the enzyme in the fruit. Using Kieffer pears, it was found that the blue color developed first around the core and immediately under the peel, but was finally developed uniformly over the freshly cut surface.

Several normal fruits were injured by passing a sharp instrument through them from side to side and allowing them to remain on the tree for forty-eight hours. A section was then made through the injury and the guaiacum solution was applied. The blue color developed first quite strongly around the walls of the injury and gradually developed in the other parts of the pear.

The ability of the enzyme to liberate oxygen from hydrogen peroxide was tested, using the apparatus described by Appleman in his work on catalase.[1] No liberation of oxygen was noted in any case.

As cold weather approached the pears were removed from the tree and stored in a cool, dry place, by which means it was hoped that the work might be continued for some time. An attempt to prepare some of the enzyme from these pears eight days after their removal from the tree

[1] *Botan. Gaz.*, 50, 162.

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resulted in a preparation which had lost practically all of its power. On testing the freshly cut surface with guaiacum solution no blue color was developed excepting rather faintly around the core.

While it is appreciated that the work as it now stands is incomplete and requires further confirmation and study, the termination of the fruit season has brought it to a close for the present and it was thought that the results obtained thus far would justify a preliminary report. It is proposed to continue the study during the coming season, when it is believed much more striking results will be obtained from the immature fruit. The present work has been done on fruit that was practically mature but there are indications that the enzyme is much more active in green fruit.

From the results now at hand we believe that the following conclusions can be drawn at least tentatively:

1. That there is present in fruits, in general, an oxidizing enzyme capable of producing a tannin-like substance having the power to precipitate protein nitrogen.

2. That this enzyme is active only in slightly acid solutions and when the concentration is above a certain minimum.

3. That this tannin-like substance or substances does not exist in the normal fruit on the tree but is rapidly formed on injury or removal of the fruit from the tree.

4. That the function of this substance or substances is to inhibit fungus and bacterial growths on injury of the fruits, in part, probably, by the conversion of the protein into an insoluble form and in part by the germicidal action of the substance itself.

It should also be stated that there are indications of another enzyme in the calcium carbonate precipitate, which is very active in liberating oxygen from hydrogen peroxide and is believed to be of the nature of a catalase. However, there has not yet been opportunity for the thorough study of this phase of the question.

We desire to express our thanks to Dr. C. F. Dawson, of this Station, who kindly prepared the cultures and offered valuable suggestions during the progress of the work.

DELAWARE COLLEGE AGRICULTURAL EXPERIMENT STATION.

[FROM THE STORRS AGRICULTURAL EXPERIMENT STATION.]

THE OCCURRENCE OF TYROSINE CRYSTALS IN ROQUEFORT CHEESE.

BY ARTHUR W. DOX.

Received January 10, 1911.

While engaged in some coöperative investigations looking toward the introduction of foreign methods of cheese manufacture into this

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country, the writer had occasion to examin many specimens of Roquefort. This variety of cheese belongs to the same general class as the Stilton and Gorgonzola types, but differs from these in the fact that it is made entirely of sheep's milk. It is characterized by its open, porous texture which permits the growth of a green mold, *Penicillium roqueforti*, through the entire mass, and the development of a peculiar pungent flavor so much admired by the connoisseur.

In the numerous cracks and crevices of this cheese, small white specks were almost invariably observed. These were especially noticeable where the air space was lined with mold, thus forming a green background. They varied in size from minute specks hardly visible to the eye to spherules the sized of a pinhead. Three possible explanations of their origin suggested themselves. It was first thought that they might consist of free fatty acids, since mold is known to possess considerable lipolytic power. Then again they might be insoluble soaps formed from the union of higher fatty acids with calcium, and lastly they might be some insoluble product of proteolysis, such as tyrosine.

With the view of determining the nature and origin of these white concretions, a number of them were laboriously picked out from a cheese in which they were particularly large and abundant, and carefully freed from the matrix of cheese. Heated on a platinum foil, they charred without melting and finally burned leaving no residue. They could therefore be neither fatty acids nor calcium soaps. They dissolved quite readily in dilute alkalies. The solution gave no biuret test but a strong Millon reaction and also Piria's test. These tests indicate a substance having a phenol group. On recrystallizing the substance from dilute ammonia water, a crystallin mass was obtained, which under the microscope was easily identified as tyrosine, from the characteristic wavy appearance of the crystals and their arrangement in bundles constricted in the middle. After purification in this way the reaction with Millon's reagent was stronger than before. Owing to the difficulty of separating these concretions from the cheese only a few centigrams were obtained—not enough for purification and analysis. Tyrosine, however, is so characteristic a substance that the above tests are sufficient for its identification. The crystals occurring in the cheese probably contain a considerable admixture of leucine.

Although white specks of this description are abundant in Roquefort, they are seldom encountered in other varieties of cheese. Van Slyke and Publow[1] note the occurrence of white specks in certain specimens of Cheddar cheese that had been ripened below the freezing point of water. They did not positively identify the material, but are inclined

[1] *Science and Practice of Cheese Making*, 1909, 332.

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toward the belief that the substance is a calcium soap, formed from fatty acids derived from the fat and the calcium salts of the cheese.

The occurrence of tyrosine in cheese is not a new observation. In Cheddar cheese it has been found by Van Slyke and Hart;[1] in Roquefort cheese by Sieber;[2] in Emmenthal cheese by Weidmann,[3] by Benecke and Schulze,[4] by Röse and Schulze,[5] by Winterstein and Thöny,[6] and in Camembert cheese by the writer.[7] In no case, however, has it been observed in the form of crystals. The peculiarity of Roquefort in this regard may be accounted for by the greater abundance of tyrosine formed and the more favorable opportunity presented for its crystallization along crevices where there is more or less circulation of air. In Swiss and Cheddar cheese tyrosine is less abundant and sometimes occurs only in traces. In both of these varieties, a decomposition product of tyrosine, *p*-hydroxyphenylethylamine, has been found. This substance results from a simple loss of carbon dioxide from the carboxyl group, a type of reaction brought about by many species of bacteria. Although *p*-hydroxyphenylethylamine has not yet been sought for in Roquefort cheese, we know that the high salt content of this variety (4 per cent. or more) very materially reduces the growth of this type of bacteria, and the tyrosine liberated by the proteolytic enzyme of the mold would be left to accumulate in the substratum until crystallization ensued.

[From the Laboratory of Physiological Chemistry of the University of Illinois.]

FASTING STUDIES: II. ON THE CATALASE CONTENT OF TISSUES AND ORGANS AFTER PROLONGED FASTING.

By P. B. Hawk.

Received January 18, 1911.

The catalytic power of pathological tissues has been studied by several investigators. For example, Jolles and Oppenheim[8] found that the blood of patients suffering from carcinoma, nephritis or tuberculosis possessed decreased catalytic power. Later it was shown by Blumenthal and Brahn[9] that secondary cancer nodules of the liver showed far less catalytic activity than normal liver tissue and, furthermore, that the liver tissue between the nodules was less active than normal liver tissue

[1] New York Agric. Expt. Sta. *Bull.* 231, 26.
[2] *J. prakt. Chem. N. F.*, 31, 203.
[3] *Landw. Jahrb.*, 11, 592.
[4] *Ibid.*, 16, 321.
[5] *Landw. Vers. Sta.*, 31, 119.
[6] *Z. physiol. Chem.*, 36, 29.
[7] Bureau of Animal Industry, *Bull.* 109, 20.
[8] *Münch. med. Wochschr.*, 1904, 47.
[9] *Z. Krebsforschung*, 8, 436.

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although more active than the cancer tissue. A sarcoma showed even less catalase than did carcinoma.

An interesting series of experiments upon the catalytic power of pathological tissues has been conducted by Winternitz and Meloy.[1] They found the catalytic values for the various tissues to vary in a pronounced manner under pathological conditions. The most marked reduction in the catalytic power of nephritic tissues was exhibited by the kidney. In eclampsia the blood showed no reduction from the normal catalase value, thus furnishing an ante-mortem medium by which eclampsia and nephritis may be differentiated. In tuberculosis the lung tissue was found to have a low catalytic power. The tissues in jaundice and diabetes mellitus exhibited no reduction in catalytic power, whereas, congenital syphilis and asphyxiation by illuminating gas produced a marked lowering of the catalase values. These investigators determined that post-mortem changes produced but a slight lowering of the catalytic power of the tissues. Their finding that the age of the subject has no material influence upon the catalytic power of the tissue is also of interest. This was shown by the fact that the tissues of a still-born infant showed normal catalytic power.

In connection with the last-mentioned finding of Winternitz and Meloy, certain experiments upon the catalase values for embryonic tissues are of interest. For example, Battelli and Stern[2] found a very low but increasing catalase value for embryonic guinea pig tissue, followed by a marked increase in the catalase content of the liver and kidney during the first week after birth. They claim a relationship between the catalytic power of a tissue and its functional activity. Buxton and Shaffer[3] likewise found that the catalytic power of embryonic tissues was always lower than that of normal tissues. On the other hand, Mendel and Leavenworth[4] working with pig embryos have determined that the catalytic power of such embryonic tissues is approximately the same as that of the adult tissue. Herlitzka[5] also reports the presence of catalase early in the development of the embryo.

The only statement as to the catalytic power of fasting tissues with which we are familiar is that made by Vernon[6] to the effect that the tissues of rats fasted from 4–8 days and the tissues of frogs fasted several months exhibited no change in catalase value. No experimental data are submitted. Vernon was likewise unsuccessful in securing any alteration in the catalytic power of the tissues of animals subjected to fatal

[1] *J. Exp. Med.*, 10, 759 (1908).
[2] *Arch. fisiol.*, 2, 471 (1905).
[3] *J. Med. Res., N. S.*, 8, 543 (1905).
[4] *Am. J. Physiol.*, 21, 85 (1908).
[5] *Biochem. Centr.*, 6, 234 (1907).
[6] Vernon, *Intracellular Enzymes*, London, 1908, 130.

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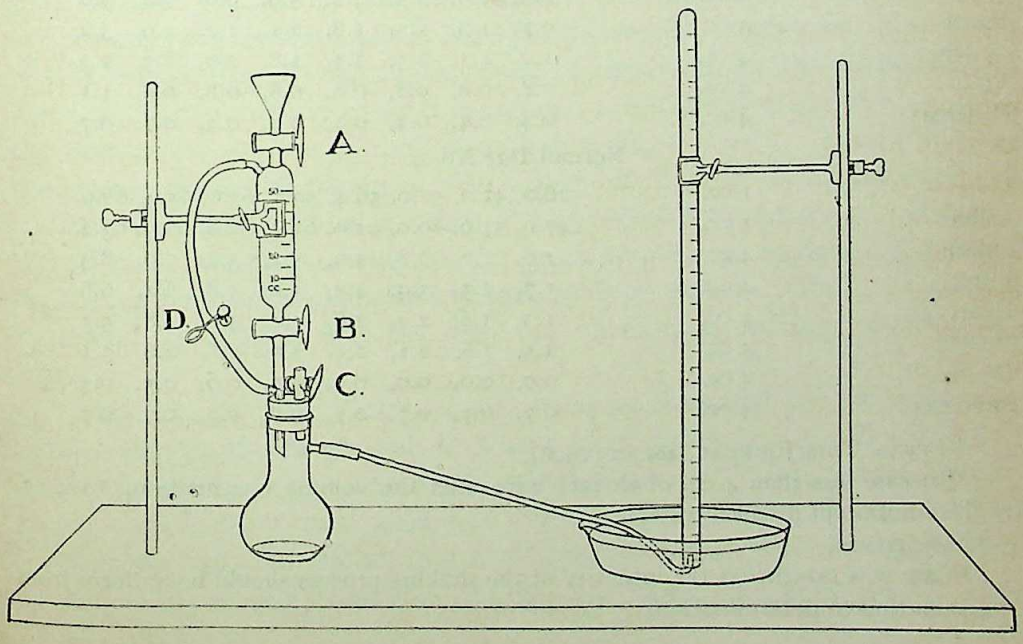
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poisoning with potassium cyanide or with phosphorus. Doses of phosphorus not sufficient to kill but large enough to produce fatty degeneration of the liver caused the catalytic power of this organ to decrease to $^1/_2$ or $^1/_3$ of its normal value.

Experimental Findings and Discussion.

In connection with our study of the alterations in catalytic power accompanying fasting the tissues and organs of four fasting dogs were utilized. Two of these animals (1 and 3) were "repeated fasters," that is, they were previously subjected to fasting periods which were carried to the premortal rise in the nitrogen excretion, then were subsequently fed through a long intermediate period until the original body weight was again assumed and finally subjected to a second fast. Of these "repeated fasters" No. 3 was a male adult animal whereas No. 1 was a female about 1–2 years of age. Dogs 2 and 6 were each subjected to but a single fast, No. 2 being a male adult whereas No. 6 was a male pup one month old. The fasting periods ranged from 7 to 104 days, being shortest for the pup and longest for the adult "repeated faster."

For the determination of the catalytic power weighed portions of the tissues under examination were ground with sand in a mortar, then treated with four volumes of chloroform water and permitted to extract for 24 hours at room temperature. From 1–4 cc. of the chloroform water filtrate was then treated with 5 cc. of hydrogen peroxide and its catalytic power, as measured by the volume of oxygen evolved through a two-minute interval, determined. An apparatus such as that reproduced in the figure was employed in determining the catalase values. The



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main features of the apparatus are based upon those of a delivery funnel for introducing liquids under increased or diminished pressure as described by Bryan.[1] A similar apparatus has been used by Dr. A. W. Peters in connection with some unpublished experiments.

In making our determinations of the catalytic power of the fasting tissues and organs a measured amount (1–4 cc.) of the extract was introduced into the small flask[2] and the modified Johnson buret graduated to 5 cc. and containing 50 cc. of hydrogen peroxide (neutralized[3] Oakland dioxygen) was introduced into the neck of the flask. The eudiometer was now properly arranged, stopcocks A and C were then closed and stopcock B and pinchcock D opened and 5 cc. of the peroxide permitted to flow into the flask. The contents of the flask were now shaken briskly,[4] and the volume of the evolved oxygen determined, readings being taken at 15-second intervals through a two-minute period. For purposes of comparison the catalytic power of the tissues and organs of two normal dogs was determined.

Normal Dogs.—In Table I are given the data upon the tissues of normal dogs Nos. 3 and 4. It will be noted that the volume of oxygen liberated by the liver extract was greater than that liberated by any other extract. The value (66.7) was however but slightly higher than that of the kidney

TABLE I.—CATALASE VALUES OF NORMAL TISSUES.

Tissue.	Volume of extract.	Volume of oxygen liberated in two minutes, cc.
	Normal Dog No. 3.	
Liver	1 cc.	47.0, 61.0, 65.0, 65.5, 65.9, 66.3, 66.3, 66.7
Kidney	1 cc.	31.0, 47.0, 57.4, 61.0, 63.5, 64.6, 65.7, 66.2
Spleen	4 cc.	0.1, 1.4, 2.2, 4.6, 6.5, 8.6, 8.9, 9.2
Lung	4 cc.	2.0, 2.9, 3.5, 4.4, 5.0, 6.0, 6.8, 7.8
Heart	4 cc.	0.7, 1.0, 1.3, 1.8, 2.1, 2.2, 2.9, 3.2
Muscle	4 cc.	1.2, 1.2, 1.5, 1.5, 1.8, 2.0, 2.3, 2.3
Brain	4 cc.	0.8, 0.8, 0.8, 0.8, 0.8, 0.8, 0.8, 1.1
Pancreas	4 cc.	0.4, 0.4, 0.4, 0.4, 0.4, 0.4, 0.7, 0.7
	Normal Dog No. 4.	
Liver	1 cc.	26.0, 42.0, 51.0, 56.4, 59.8, 63.6, 65.4, 66.6
Kidney	1 cc.	47.0, 57.0, 60.0, 61.0, 62.2, 62.6, 62.9, 63.2
Spleen	4 cc.	1.6, 2.2, 2.8, 4.0, 5.2, 5.8, 7.0, 8.3
Lung	4 cc.	1.7, 2.5, 3.9, 4.3, 5.2, 5.8, 6.4, 6.6
Heart	4 cc.	1.3, 1.6, 2.2, 2.8, 3.4, 4.1, 4.8, 5.3
Muscle	4 cc.	1.5, 1.8, 2.1, 2.4, 2.6, 2.6, 2.8, 3.1
Brain.	4 cc.	0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.5, 0.5
Pancreas	4 cc.	0.7, 0.7, 0.7, 0.7, 0.7, 0.7, 0.7, 0.7

[1] Bryan, THIS JOURNAL, 28, 80 (1906).

[2] In case less than 4 cc. of extract were used the volume was made up to 4 cc. by the addition of distilled water.

[3] Congo red.

[4] Care was taken that the intensity of the shaking process should be uniform from determination to determination.

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tissue (66.2). With the exception of the liver and kidney the other tissues examined showed low values, the spleen (9.2) and lung (7.8) being highest and the brain (1.1) and pancreas (0.7) being lowest. The values for the tissues of normal dog No. 4 are very closely comparable with those for the tissues of normal dog No. 3 just considered. The liver for example gave a figure (66.6) which was practically the same as that of dog No. 3 whereas the kidney was but slightly lower with a value of 63.2. As was the case with the other normal animal the liver and kidney possessed much higher catalytic power than did the other normal tissues examined. The spleen and lung tissue again came next in order after the liver and kidney in so far as their catalytic activity was concerned.

The average catalase values for these normal animals calculated on the basis of the different determinations are given in Table IV, p. 432. An examination of this table will show the average values for normal dog tissues to be as follows: liver 67.1, kidney 64.9, spleen 8.8, lung 7.2, heart 4.3, muscle 2.7, brain 0.8, and pancreas 0.7.

Fasting Dog No. 3.—In Table II are tabulated the data from the tissues of fasting dogs Nos. 3 and 2. Dog No. 3 the year previous to the final fasting test had been subjected to a fast of 117 days, this being by many days the longest fast on record. Some features of this fast have already been reported.[1] Following this record-breaking fast the animal was carefully fed and gradually brought back to his normal condition. He was then subjected to a second fast of 104 days at the end of which time his tissues were examined as to their catalytic power. If the withdrawal of food from an animal for a period is to exert any influence upon the catalytic power of the tissues of that animal we certainly would expect that fasts of the nature just described would accomplish such a result. We consider it decidedly surprising that the catalase values for the tissues of this animal were so nearly like those of the tissues of the normal dogs. For example the liver was 52.0 as against a normal average of 67.1, and the kidney was 50.7 as against a normal average of 64.9. Then followed the spleen, heart and pancreas with values but slightly lower than normal values. The lung yielded a value of 10.8 which was nearly 50 per cent. higher than the normal whereas the brain was 8.2 as against 0.8 a most surprising increase of eight-fold in the catalytic power. Of all the tissues examined the muscle was the only one showing entire loss of catalytic power.

A close comparison of the oxygen volumes liberated by the liver and kidney tissues of the normal dogs and fasting dog No. 3 will exhibit a most interesting fact. The total volumes are very closely comparable as has already been mentioned, yet when we examin into the rate of the reaction we find that the oxygen was liberated much more slowly through

[1] Howe, Mattill and Hawk, *Proc. Am. Soc. Biol. Chem.*, June, 1910, 260.

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the medium of the catalase of the fasting tissues than through the medium of the catalase of the normal tissues. Under normal conditions 40–75 per cent. of the total volume of oxygen liberated in a two-minute period from 5 cc. of hydrogen peroxide through the catalytic power of 1 cc. of liver or kidney extract was evolved in the first 15 seconds. In the case of the tissues of fasting dog No. 3 the volume of oxygen liberated under the same conditions and in a similar time interval was only 16–36 per cent. of the total volume liberated. In other words although the catalytic powers of the tissues of the normal and fasting dogs were rather closely comparable from the standpoint of the total volume of oxygen liberated there were striking differences in the velocity of the reaction. The rate was less rapid during the first part of the two-minute interval in the case of fasting tissues and more rapid during the second part than was the rate in the case of the normal tissues.

TABLE II.—CATALASE VALUES OF FASTING TISSUES.

Tissue.	Volume of extract.	Volume of oxygen liberated in two minutes, cc.
		Fasting Dog No. 3.
Liver	1 cc.	8.4, 14.2, 23.4, 34.2, 42.1, 47.2, 50.5, 52.0
Kidney	1 cc.	18.4, 25.0, 32.7, 39.9, 44.2, 47.5, 49.4, 50.7
Spleen	4 cc.	0.9, 1.2, 1.7, 2.3, 2.5, 3.4, 4.2, 5.1
Lung	4 cc.	1.5, 2.7, 3.7, 5.2, 6.5, 7.8, 9.0, 10.6
Heart	4 cc.	0.4, 0.8, 1.0, 1.3, 1.5, 1.8, 2.0, 2.6
Muscle	4 cc.	negative
Brain	4 cc.	1.6, 2.8, 3.9, 4.8, 5.9, 6.5, 7.3, 8.2
Pancreas	4 cc.	0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.5
		Fasting Dog No. 2.
Liver	1 cc.	2.1, 4.1, 6.5, 9.9, 12.9, 16.2, 19.6, 23.0
Kidney	1 cc.	0.5, 0.8, 1.2, 1.6, 2.1, 2.8, 3.5, 4.4
Spleen	4 cc.	negative
Lung	4 cc.	1.2, 2.3, 3.0, 4.6, 5.2, 6.3, 7.1, 8.2
Heart	4 cc.	negative
Muscle	4 cc.	negative
Brain	4 cc.	negative
Pancreas	4 cc.	negative

The relative order of the tissues when placed according to their catalase values was rather different for fasting dog No. 3 than for the normal animals. This may be seen by examining Table V. The order as determined for the normal animals was liver, kidney, spleen, lung, heart, muscle, brain and pancreas. In the case of the faster the liver and kidney still retained their preëminent positions and the pancreas was still at the end of the list but the intermediate positions of lung, spleen, brain and heart were rearranged. The order of tissues for this dog was liver, kidney, lung, brain, spleen, heart and pancreas.

Fasting Dog No. 2.—When we come to consider this animal we find a condition decidedly at variance with what we have already observed

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in the case of the repeated faster just discussed. For example a value of 23.0 is registered for the liver as against 52.0 for fasting dog No. 3, a value of 4.4 is registered for the kidney as against 50.7 and the only other tissue which showed any catalytic power was the lung which gave a value of 8.2. It will be noted that the catalase value of the lung tissue was above that of kidney tissue, this being the sole instance during the series of studies in which this relative order was observed. The significance of the pronounced variations between the catalase values for the tissues of the two fasting dogs under consideration will be further emphasized when it is remembered that they were both adult animals, one of them (No. 2) an "initial faster" the other (No. 3) a "repeated faster." One characteristic was possessed in common by the tissues of these two fasters. This relates to the velocity of the reaction by which the oxygen was evolved. Here again as was shown in the case of fasting dog No. 3 the liberation of oxygen was much slower than normal during the first part of the 2-minute interval, a condition which was followed by a compensating acceleration during the second part of the period.

Fasting Dog No. 1.—Here for the first time we have a catalase value for kidney tissue above that for the liver tissue of the same animal. This may be observed if Table III be examined, the recorded catalase value for liver tissue being 34.7 as against the higher one of 47.9 for kidney

TABLE III.—CATALASE VALUES OF FASTING TISSUES.

Tissue.	Volume of extract.	Volume of oxygen liberated in two minutes, cc.
Fasting Dog No. 1.		
Liver	1 cc.	1.2, 2.3, 4.6, 9.6, 16.1, 21.6, 29.2, 34.7
Kidney	1 cc.	7.2, 18.9, 32.4, 41.1, 45.0, 46.6, 47.6, 47.9
Spleen	4 cc.	negative
Lung	4 cc.	0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.5, 0.5
Heart	4 cc.	negative
Muscle	4 cc.	negative
Brain	4 cc.	negative
Pancreas	4 cc.	negative
Fasting Dog No. 6.		
Liver	1 cc.	2.0, 19.0, 28.1, 41.5, 50.8, 54.8, 56.2, 57.0
Kidney	1 cc.	0.8, 1.3, 2.3, 3.6, 4.9, 7.0, 8.7, 11.1
Spleen	4 cc.	not examined
Lung	4 cc.	0.0, 0.5, 0.5, 0.5, 0.5, 0.9, 0.9, 1.2
Heart	4 cc.	0.9, 1.4, 2.2, 3.4, 4.9, 7.2, 9.6, 12.3
Muscle	4 cc.	negative
Brain	4 cc.	negative
Pancreas	4 cc.	negative

tissue. In common with dog No. 2 this animal showed absence of catalytic power in all but three tissues, the third tissue in connection with which catalytic power was demonstrated being the lung. With the exception of the lung value the tissues of dog No. 1 showed stronger catalytic

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power than did the tissues of dog No. 2, the average value for the kidney tissue being 46.5 (Table IV) as compared with 4.4 for the last mentioned animal.

In line with the conditions in force with the other fasting dogs the evolution of the oxygen was less rapid during the first part of the experimental period and more rapid during the second part of this period than was the case with the normal dogs.

Fasting Dog No. 6.—Here we are dealing with a pup only one month old, and for this reason the data cannot logically be compared with those obtained from the analysis of the tissues of the other animals. Tables III and IV show that the value for liver tissue (57.0) was approximately normal. Kidney tissue however yielded a catalase value of only 11.1 which is the second lowest kidney value secured. One of the striking features of the tissue examination in the case of this animal was the high catalase value for heart tissue, this being 12.3, which was about 3 times as great as that of normal heart tissue and also slightly above that of the kidney tissue of the same animal. In the relative order of the tissues for this animal the heart tissue therefore comes second as may be seen in Table V. Here again we note the slow rate of the catalytic action as compared with that for normal tissues.

TABLE IV.—AVERAGE CATALASE VALUES.

	Tissue.								
Dog.	Liver.	Kidney.	Spleen.	Lung.	Heart.	Muscle.	Brain.	Pancreas.	Days.
Normal	67.1	64.9	8.8	7.2	4.3	2.7	0.8	0.7	...
Fasting (3)	52.7	50.4	5.1	10.8	2.6	0.0	8.2	0.5	104
Fasting (2)	23.8	4.4	0.0	8.2	0.0	0.0	0.0	0.0	48
Fasting (1)	34.8	46.5	0.0	0.5	0.0	0.0	0.0	0.0	30
Fasting (6)	57.0	11.1	...	1.2	12.3	0.0	0.0	0.0	7

TABLE V.—RELATIVE ORDER OF TISSUES.

Normal	Liver	Kidney	Spleen	Lung	Heart	Muscle	Brain	Pancreas	...
Fasting (3)	Liver	Kidney	Lung	Brain	Spleen	Heart	Pancreas		104
Fasting (2)	Liver	Lung	Kidney						48
Fasting (1)	Kidney	Liver	Lung						30
Fasting (6)	Liver	Heart	Kidney	Lung					7

General Considerations.—A general conclusion to be drawn after a careful examination of all data submitted is to the effect that fasting tended to *lower* the catalytic power of the animal tissues under examination. There were certain isolated instances however in which the fasting régime tended to increase the catalytic power. It may further be stated as demonstrated that there was no regularity in the extent to which the catalytic power of a given tissue from different animals was lowered.

Of the four fasting animals examined two may be directly compared inasmuch as they were adult animals. These are Nos. 2 and 3. When we compare the data from the examination of the tissues of these two

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dogs as given in Table IV, we are confronted by very striking variations. Dog No. 2 showed entire absence of catalytic power in 5 of the 8 tissues examined and furthermore of the 3 tissues which contained catalase the maximum value was 23.8 for liver tissue, a value which was only about $^1/_3$ that of normal tissue. The kidney value was the surprisingly low one of 4.4, a value only 7 per cent. as great as that shown by normal tissues. Now turning to the other adult animal (dog No. 3) we observe that the values throughout are not far removed from the normal, the data showing slightly lower catalase values in five tissues, higher in two tissues and entire absence of a catalytic power in but a single tissue.

Why do we find these pronounced differences in the catalase values for the tissues of these two adult fasting dogs? The answer we believe is centered in the fact that in one case we are dealing with a dog fasting for the first time whereas in the other case we are dealing with a "repeated faster."

When we are considering the close agreement between the catalase values for the tissues of fasting dog No. 3 and those of the normal animals we must not forget that we are here dealing not with an ordinary fasting dog but rather with an animal which had undergone two very long fasts. We venture to assert, and we believe certain of our other data will bear us out in the assertion, that had this dog been killed at the end of his first fast and the catalytic power of his tissues determined, the values would have been much lower and more widely at variance with the normal than were these values as determined by us at the end of his second fast.

Our experiments upon "repeated fasters"[1] have led us to the conclusion that the animal organism is in much better condition, from all observable standpoints, at the end of a second fast than at the end of the original fast provided that during the intermediate period the animal be fed carefully and restored as nearly as possible to the physical condition in force before the initial fast. This is true even though the repeated fast be of longer duration than the original fast.

We believe that an animal organism which has once been subjected to a severe fast acquires from this fact a kind of *immunity or resistance* which enables such an organism to more successfully cope with the problems of the abnormal fasting condition as they arise and that this and other associated factors permits the animal to regulate its varied activities more efficiently and to make a more economical utilization of the available body tissues. We expect to further investigate the question of a possible fasting immunity or resistance.

Whether or not the suggestions as to the fasting immunity or resistance are generally accepted, the central and important fact, determined by actual experimentation, still remains. This is the observation that *the*

[1] Howe and Hawk, THIS JOURNAL, 33, 215 (1910).

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tissues of an adult dog which had been subjected to two fasts of 117 days and 104 days in duration respectively, possessed catalytic powers which were much more comparable with the catalytic powers of normal tissues than with the catalytic powers of the tissues of another adult dog which had been subjected to but a single fast 48 days in length. Arguments against drawing any important conclusions from these facts may of course be adduced from the standpoint of individuality. However, in view of other related data already mentioned as obtained from repeated fasters[1] we are willing to stand upon our interpretation. That our data upon catalase values may properly be interpreted as indicating the efficacy of "repeated fasting" is brought out still more clearly in connection with the work of Battelli and Stern[2] in which they determined that the catalytic power of the tissues was an index of functional activity. On the basis of this finding, therefore, our observation of higher catalase values for the tissues of adult "repeated fasters" as compared with adult "initial fasters" may be taken as indicating the more efficient functional activity of the repeated faster.

[Contribution from the Department of Chemistry, Indiana University.]

THE DECOMPOSITION OF URIC ACID BY ORGANIC ALKALINE SOLVENTS.

By Hannah Stevens and Clarence E. May.

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From time to time, there have appeared in the literature statements regarding the decompositions uric acid underwent when exposed to the action of alkaline inorganic solvents. Various chemists, Austin, Schittenhelm, Folin and others have noted a loss of uric acid while using an alkali, such as sodium hydroxide, as solvent. Austin has quite conclusively shown the effects of inorganic alkalis in splitting uric acid. He digested solutions of uric acid in Na_2CO_3, Li_2CO_3, Na_2HPO_4 and NaOH respectively for different periods of time and at different temperatures. He proved beyond a doubt that uric acid was destroyed by alkalies, even when acting in the cold, and that this destruction was greatly increased when the temperature was increased to that above room temperature. Sodium hydroxide was found to be by far the most active, for although a solution of only 0.024 gram NaOH per 400 cc. of water was allowed to act on some of the acid, he was able to recover only about 50 per cent. of his acid. Sodium carbonate proved to be least destructive. Schittenhelm also, in using sodium hydroxide as a solvent lost about one-sixth of his uric acid. Further, Folin found that uric acid was decom-

[1] Howe and Hawk, *loc. cit.*

[2] Battelli and Stern, *loc. cit.*

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posed fairly quickly by the action of ammonium hydroxide and that the presence of ammonium salts prevented this destruction. He made use of this deportment in determining uric acid as ammonium urate by precipitation with ammonium hydroxide in the presence of another ammonium salt, preferably the sulfate.

It has been the purpose of this series of experiments to determin the stability of uric acid in some few organic alkaline solvents and where there was decomposition, to ascertain whether it reached a maximum at which all further action ceased, or whether it continued to increase from day to day; also to determin whether an increase in the concentration of the solvent affected in any marked way the stability of uric acid in that particular solvent. No attempt has been made to bring out the effect of heat on this destructive property, as all experiments were carried on at room temperature. There has also been no effort made to study the cleavage products formed in the decomposition and only such facts are known about them as were incidentally brought to notice during this investigation.

The uric acid used was some that had been purified by dissolving in dilute sodium hydroxide and reprecipitating by the passage of CO_2 through the solution. This residue was thoroughly washed and dried and was found to be ash-free and quite pure, as was indicated by ignition of some of the material and by a Kjeldahl nitrogen determination. This uric acid sample was used in the first two piperazine solutions, that used in the other experiments was a preparation of Merck's.

The Folin-Schaffer method of uric acid determination was taken as the standard method throughout this work. This method depended on taking a 100 cc. portion of the uric-acid-bearing material, and treating it with 25 cc. of the Folin-Schaffer reagent (a solution composed of 500 grams ammonium sulfate and 5 grams uranium acetate together with 60 cc. of 10 per cent. acetic acid in 650 cc. of water). On the addition of this reagent the mixture was filtered and the filtrate was allowed to stand twenty-four hours. The uric acid that separated was filtered and washed with 10 per cent. ammonium sulfate, then dissolved with hot water, filtering into the original beaker. After the addition of 15 cc. of conc. sulfuric acid, the mixture was titrated against a 0.05 *N* $KMnO_4$ solution. Each cubic centimeter of the permanganate corresponded to 0.00375 gram uric acid. When there was any deviation from this method of procedure, it will be noted.

The solvents used were piperazine, urotropin and lycetol. Of these, piperazine was by far the best solvent and there was no difficulty in making a solution of any strength desired. The solubility of piperazine urate is given in the literature as 1 : 50 in water at 17°. Urotropin was

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found to be only a fair solvent. The maximum amount of uric acid that we found would dissolve in a liter of water containing 15 grams urotropin, at room temperature, was 0.35 gram. Larger amounts refused to dissolve completely. At room temperature, lycetol was a very poor solvent of uric acid since no appreciable quantity of the acid could be made to dissolve. In a hot solution a small quantity dissolved yet it was immediately precipitated again on cooling.

Each stock piperazine solution was made up by dissolving the given weight of uric acid in cold water in a graduated flask into which a weighed amount of piperazine had been placed. This solution together with washings was filtered into a graduated flask and diluted immediately to the mark. Samples of 100 cc. each were taken from day to day and the uric acid content was determined by the Folin-Schaffer method. Washings of 100 cc. 10 per cent. $(NH_4)_2SO_4$ were used and the final residue was taken up in about 150 cc. boiling water; after the addition of 15 cc. concentrated sulfuric acid, the mixture was titrated with standard permanganate. When the uric acid residue was dissolved in hot water prior to titration, there was always a yellow residue left on the paper. No attempt was made to determin the nature of this residue. No account was taken of the loss of uric acid through washing, as the error made in this way was uniform in each case and the estimated amount of uric acid destroyed was independent of this small loss.

TABLE I.—TWO GRAMS URIC ACID DISSOLVED IN 2000 CC. WATER CONTAINING SIX GRAMS PIPERAZINE.

	I. 2 days.	II. 6 days.	III. 8 days.	IV. 12 days.	V. 15 days.	VI. 21 days.	VII. 29 days.	VIII. 36 days.	IX. 43 days.
Cc. $KMnO_4$ used in titration of	2.0	19.2	15.8	7.0	1.0	8.5	5.5	6.3	5.5
duplicates	2.0	19.2	15.8	...	0.8	8.4	6.1	6.3	...
Grams uric acid recovered in	0.0557	0.0534	0.0443	0.0185	0.0026	0.0224	0.014	0.023	0.0204
duplicates	0.0557	0.0534	0.0443	....	0.0021	0.0223	0.016	0.023	....
Gms. uric acid the solution should	0.08	0.0856	0.0856	0.08	0.0856	0.08	0.08	0.08	....
have contained (in duplicate)	0.08	0.0856	0.0856	....	0.0856	0.08	0.08	0.08	....

DUPLICATE OF TABLE I.

	I. 2 days.	II. 6 days.	III. 8 days.	IV. 13 days.	V. 15 days.
Cc. $KMnO_4$ consumed (duplicates)	18.1	15.0	14.1	10.3	9.8
	18.1	15.0	14.2	10.5	9.8
Grams uric acid recovered (in duplicate)	0.0662	0.055	0.051	0.0377	0.0359
	0.0662	0.055	0.052	0.0398	0.0359
Grams uric acid the solution should have contained (in duplicate)	0.08	0.08	0.08	0.08	0.08
	0.08	0.08	0.08	0.08	0.08

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TABLE II.—TWO GRAMS URIC ACID DISSOLVED IN 2000 CC. WATER CONTAINING FOUR GRAMS PIPERAZINE.

	I. 1 day.	II. 4 days.	III. 7 days.	IV. 13 days.	V. 20 days.	VI. 27 days.	VII. 34 days.
Cc. $KMnO_4$ consumed (duplicates)	18.2	14.1	3.4	13.6	10.8	9.2	6.2
	10.6	18.7	3.7	13.6	11.0	10.9	7.0
Grams uric acid recovered (duplicates)	0.0507	0.0352	0.0089	0.0359	0.0285	0.0342	0.0231
	0.0293	0.0494	0.0095	0.0359	0.0290	0.0400	0.0260
Grams uric acid the solution should have contained (duplicates)	0.0856	0.08	0.0856	0.08	0.08	0.08	0.08
	0.0856	0.08	0.0856	0.08	0.08	0.08	0.08

TABLE III.—TWO GRAMS URIC ACID IN 500 CC. WATER CONTAINING SIX GRAMS PIPERAZINE.

	I. 3 days.	II. 9 days.	III. 13 days.	IV. 17 days.	V. 22 days.
Cc. $KMnO_4$ consumed (duplicates)	24.0	22.1	19.9	18.6	15.3
	23.9	22.0	20.0	18.4	15.4
Grams uric acid recovered (duplicates)	0.088	0.081	0.0733	0.068	0.059
	0.087	0.080	0.0729	0.068	0.0579
Theory	0.1	0.1	0.1	0.1	0.1
	0.1	0.1	0.1	0.1	0.1

In Series I, II and III in Table I, the permanganate solution was 0.74375 $N/20$. It was found that the uric acid had a tendency to separate from solution after the addition of the Folin-Schaffer reagent, so dilution with 50 cc. of water was tried at this stage and an aliquot portion of the resulting mixture (100 cc.) was used. In II, III and V, this dilution was made but as it did not seem to affect the crystallization, it was abandoned without further trial. In IV, V, VI and VII, 0.73155 $N/20$ $KMnO_4$ was used. In IV, one sample was lost entirely and freshly prepared Folin-Schaffer reagent was used in which all the ammonium sulfate had not dissolved. This lack of ammonium sulfate might possibly account for the results obtained. In VIII and IX, 0.99416 $N/20$ $KMnO_4$ was used. In IX, also only one sample was taken, hence the blank in the table. In the duplication of this work (Table I) the amount of uric acid found uniformly ran higher. This might be accounted for by the fact that a different preparation of uric acid was used. There was also no tendency of the acid to crystallize out as in the first work. The permanganate used was 0.978 $N/20$.

In Table II, the permanganate used was 0.743575 $N/20$ in I, 0.73155 $N/20$ in II, III, IV, and V, 0.99416 $N/20$ in VI and VII. In I and II, dilution was made to prevent the crystallization of the uric acid but nothing was gained; the uric acid continued to separate from solution.

In Table III, since a quite concentrated solution was being used, it was necessary to follow a slightly different treatment. Only 25 cc. portions were pipetted out and these were diluted to 225 cc. to prevent the precipitation of the uric acid on the addition of the Folin-Schaffer

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reagent. The amount of this reagent was 30 cc. instead of 25 cc. as in the former work. It was found that with solutions of this concentration, unless this precaution of dilution was taken the uric acid was completely thrown out of solution on the addition of the reagent. Sufficient dilution prevented any precipitation whatever and it was not necessary to filter in this case.

The amount of ammonium hydroxide was increased from 5–10 cc. in order to keep a constant ammonium hydroxide concentration. The residue was taken up in 200 cc. boiling water and acidified with 30 cc. concentrated sulfuric acid before titration.

On examination of these tables, it is evident that uric acid was attacked in a piperazine solution. In all three solutions of different strengths there were losses of uric acid that can be accounted for in no way except through the action of piperazine. Conditions were uniform in every case and any error in the method would remain constant throughout. Even with only two days' action, there was quite an appreciable loss of uric acid. These experiments extended over periods of from one to forty-two days and in the main the decomposition seemed to gradually continue throughout the period of the investigation. We found on maximum beyond which all action ceased.

A comparison of the concentrations of the piperazine solutions will show that the solution used in Table III was just twice as great as that of the solution used in Table I. The solution used in Table II was weaker than either of the former. The amount of uric acid involved was the same in each case. Corresponding to the difference in concentration of the solvent, no change in the amount of uric acid recovered was noted. This amount grew uniformly less in all three cases, according to the time through which action was allowed to continue. There was no marked increase in the decomposition induced by the increased piperazine concentration, but it continued at about the same rate in all cases. The destruction seemed to continue independent of the concentration of the solvent.

The second solvent whose destructive action on uric acid was studied was urotropin. As stated previously this did not prove to be a very good solvent and even in small quantities, with a reasonably concentrated solution of urotropin, considerable agitation was necessary to effect solution. In the first solution the attempt was made to dissolve 1 gram of uric acid in one liter of water containing 10 grams urotropin. Only a small fraction of the acid dissolved and it was necessary to filter into a flask and take samples immediately in order to determin how much uric acid had gone into solution.

The same method was followed in this work as in the work with piperazine except that it was necessary to filter on the addition of the Folin-

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Schaffer reagent to some of the piperazine urate solutions while in the case of the urotropin solutions, it was never necessary to filter the solution at this stage. A yellow residue insoluble in hot water was obtained on the final precipitation of uric acid as ammonium urate. Solutions of only two different concentrations were studied but the results obtained were sufficient to indicate the action. The following tables show the results obtained.

TABLE IV.— LESS THAN ONE GRAM URIC ACID DISSOLVED IN 1000 CC. CONTAINING 10 GRAMS UROTROPIN.

	I. 1 day.	II. 7 days.	III. 14 days.
Cc. $KMnO_4$ consumed (triplicates)	3.8	3.8	3.8
	3.8	3.8	3.8
	3.5	3.8	3.8
Grams uric acid recovered	0.0137	0.0137	0.0137
	0.0137	0.0137	0.0137
	0.0128	0.0137	0.0137

TABLE V.—0.1 GRAM URIC ACID IN 400 CC. WATER CONTAINING 6 GRAMS UROTROPIN.

	I. 7 days.	II. 14 days.
Cc. $KMnO_4$ consumed (duplicates)	4.4	4.6
	4.6	4.6
Grams uric acid recovered	0.0161	0.0168
	0.0168	0.0168
Theory	0.02	p.02
	0.02	0.02

From the results it seemed that urotropin had no effect on uric acid under the conditions employed. In the first case where the exact acid content was not known, samples were taken the same day. Those taken a week and even two weeks later showed exactly the same amount of uric acid present as there was in the first place. There could have been no destructive action exerted by the urotropin. In the second solution, no sample was taken the first day, as the exact uric acid content was known; but after seven and fourteen days respectively there was still the same amount of acid present. The titration does not check with the actual amount of uric acid known to have been present, but if the correction is made for the solubility of uric acid in washings, etc., part of this loss may be accounted for. There was a 100 cc. filtrate on the precipitation of uric acid with ammonium hydroxide and 100 cc. 10 per cent. ammonium sulfate solution were used in washing.

The strength of the urotropin solution did not seem to affect the destruction of uric acid to any marked extent. An increase of 5 grams solid urotropin per 1000 cc. of solution brought the same results as far as destructive action was concerned. Basing conclusions on these results, it would seem that in cold solutions urotropin did not have the power of

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splitting uric acid. Further, the concentration of the solvent in no way changed its action on uric acid to bring about decomposition under such conditions as were used.

Decompositions by Means of Ammonia.—After studying the extent of action of a few alkaline solvents on uric acid, it seemed desirable to study the action of ammonia with regard to the decomposition it may bring about with uric acid, both in the presence and absence of ammonium salts. That ammonia alone has the power to split uric acid is quite well known. A few experiments were made in this laboratory to gain some idea of the extent of its decomposition at room temperature. Dilute ammonia (1 per cent.) was used in one instance in an attempt to dissolve 1 gram of the acid. The ammonium hydroxide was added to small portions of the acid at a time so that the disappearance of the acid would show that some small amount had dissolved. The uric acid was only slightly soluble in ammonium hydroxide. The solution was filtered and 100 cc. samples were taken the same day. It was found that on the addition of the Folin-Schaffer reagent a heavy white precipitate separated and no further precipitate could be obtained after filtering, on the addition of concentrated ammonia. To prevent the separation of the acid on the addition of the reagent, the solution was barely neutralized with acetic acid. After this treatment no precipitate at all was formed. The entire solution was then treated with 5 cc. of concentrated ammonium hydroxide. At this stage there resulted a heavy yellowish precipitate that for the most part was soluble in hot water, a condition quite contrary to that obtained when piperazine and urotropin were used as solvents. This residue was practically completely dissolved in 100 cc. of boiling water and on titrating with permanganate only three drops sufficed to give a very distinct color to the solution, thus showing that practically all the uric acid had disappeared prior to the titration. The heavy precipitate previously mentioned must have been a decomposition product of uric acid; at any rate, the substance did not consume permanganate to any extent.

A second solution of 1 per cent. ammonium hydroxide was made to completely dissolve 0.2 gram uric acid. This was best accomplished by agitation and by the addition of ammonium hydroxide in small quantities and decanting off from time to time to a graduated flask. Samples of this solution were run the next day with exactly the same result as before. The entire amount of uric acid as such had disappeared, since three drops of the standard permanganate solution produced a permanent color.

The next phase of the work had to do with the determination of uric acid in silver magnesium urate by the common methods and another method involving the use of ammonia. Having noted the use of sodium

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sulfide in place of hydrogen sulfide in the decomposition of silver urate (the Salkowski modification of the Ludwig H_2S-silver urate method for the determination of uric acid) it seemed desirable to prepare some silver magnesium urate and allow weighed quantities of this urate to be acted on respectively by H_2S, Na_2S and $(NH_4)_2S$.

In the preparation of this silver urate about 10 grams of Merck's uric acid were dissolved in the least quantity of cold dilute sodium hydroxide necessary for complete solution. The resulting solution, about one liter in volume, was filtered into a tall gas generator cylinder and was treated with equal volumes of magnesia mixture and ammoniacal silver nitrate as long as a heavy white precipitate settled out. The mixture was allowed to stand until the precipitate of silver magnesium urate settled. The supernatant liquid was siphoned off, replaced by dilute ammonia, stirred, allowed to settle and the second supernatant liquid was siphoned off. This was the best way we found for washing the precipitate free from impurities so this washing procedure was repeated several times. The white precipitate was filtered by means of suction, using a porous plate, and dried. The dry urate was pulverized in a mortar and run through a 100-mesh sieve. To insure like conditions up as far as the treatment with the respective sulfides, the urate thus obtained was used as starting material. This was granular, finely divided and a pure white color.

The magnesia mixture contained 100 grams magnesium chloride dissolved in dilute ammonium hydroxide and treated with solid ammonium chloride sufficient to dissolve the precipitate formed. The resulting mixture was diluted to one liter.

The ammoniacal silver nitrate was made as follows: 26 grams of silver nitrate were dissolved in water and enough ammonium hydroxide was added to completely dissolve the precipitate formed. The solution was then diluted to one liter.

The sodium sulfide used in the Salkowski modification of the Ludwig H_2S method was made by dissolving 10 grams of sodium hydroxide in a liter of water. One-half of this solution was saturated with hydrogen sulfide and then mixed with the other half of the solution.

After the preparation of several grams of the silver magnesium urate the three reagents H_2S, Na_2S and $(NH_4)_2S$ corresponding to the Ludwig, Salkowski and the authors' methods respectively were allowed to react to precipitate silver as the sulfide and liberate the uric acid in a separable form.

The Ludwig Method.—In this method 0.2 gram of our urate was accurately weighed and placed in a beaker containing 100 cc. water. The mixture was heated to near boiling and allowed to react while still hot with a current of hydrogen sulfide. The heating and passage of the gas

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was continued for several minutes. During this time the white gritty precipitate was replaced by the usual black silver sulfide precipitate. However it was only after repeated heatings and saturations with hydrogen sulfide that the complete conversion of silver urate to silver sulfide was brought about. The resulting solution was filtered and the residue was washed with hot hydrogen sulfide water. On evaporation to about 100 cc. volume and acidification with a few drops of concentrated hydrochloric acid, a heavy white precipitate of uric acid separated. On standing over night the solution yielded more uric acid that was filtered and washed slightly with 100 cc. cold water. By means of hot water the uric acid precipitate was allowed to dissolve and drain back from the filter to the original precipitation beaker. After adding 30 cc. concentrated sulfuric acid the resulting slightly warm solution was titrated immediately with a standard permanganate solution.

By the Salkowski-Ludwig method, weighed quantities of the urate (0.2 gram) were suspended in 100 cc. portions of water in respective beakers. On being heated to near boiling the mixtures were treated with the sodium sulfide solution until an excess was present. This was indicated by the odor. The mixture was maintained at near boiling on a water bath for ten minutes. Meanwhile, by gradual stirring with a rod, the granules were broken up and more thoroughly converted to sulfide. The black solution was then filtered and given the same treatment as in the case of the use of the Ludwig method.

By the general deportment of ammonia and uric acid, it was suspected that ammonium sulfide used to replace sodium or hydrogen sulfide might have a tendency to cause the loss of some uric acid in any determination employing that reagent. Hydrogen sulfide seemed to us to not act vigorously enough in the conversion of silver urate to silver sulfide. The sodium sulfide method, while getting around the problem of complete conversion of sulfide, introduced an error due to the subsequent action of the alkali on the uric acid. Thinking the use of ammonium sulfide would get around this alkaline decomposition at least to an extent worthy of a method, the authors developed and used the following method with more or less success.

Equal portions of the urate were suspended in about 100 cc. of water and treated with ammonium sulfide until the mixture smelled strongly of ammonia. (The sulfide was the ordinary yellow sulfide; the amount of silver urate used in all cases was 0.2 gram.) The solution was then heated on a water bath for about 10 minutes with constant stirring until the silver was completely precipitated as silver sulfide. This was shown by the thorough blackening of the precipitate and the change from a granular to a flocculent form. The solution was allowed to cool slightly and then filtered. The residue was washed with boiling water until the total

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volume of the filtrate was about 300 cc. A few drops of concentrated hydrochloric acid were added to the filtrate and this was concentrated to about 75 cc. when 15–20 drops more of hydrochloric acid were added and the solution was allowed to stand 18 hours when it was filtered. It was at this point that the difficulty in the process arose. On account of the excess of sulfur that had separated from solution, it was found impossible to dissolve all the uric acid in hot water. The sulfur seemed to prevent the contact between uric acid and water and it also prevented sharp end points in the subsequent titrations. Hence a scheme was devised to eliminate the sulfur by a mixed solvent in which uric acid was insoluble. Some work was done using carbon disulfide alone as a solvent but it was found that a mixture of equal parts carbon disulfide and chloroform seemed better as a sulfur solvent under the conditions. (By actual test under similar titration conditions sulfur did not consume permanganate nor have any influence on the sharpness of the end point. Uric acid mixed with sulfur gave a very uncertain end point with permanganate.)

The uric acid sulfur residues were washed with hot water and the washings were allowed to reach a maximum volume of 100 cc. Then the precipitation beaker still containing some sulfur and uric acid and the filter containing the main portion of the precipitate were dried thoroughly. The sulfur was then dissolved by means of 75–100 cc. of CS_2–$CHCl_3$ mixture that had been heated almost to its boiling point. The washings were discarded and the beaker and filter were again dried thoroughly. After this treatment the uric acid could easily be taken up in boiling water and titrated. Sharp end points were almost always obtained. Just before the addition of any permanganate the uric acid was dissolved in dilute potassium hydroxide. This was necessary for a sharp end point in the titration.

After working out the details for the determination of uric acid by each of the three methods, equal weighed quantities of the magnesium silver urate were taken and in these samples the uric acid was determined four times by each method, besides two determinations by the authors' method using carbon disulfide alone as a sulfur solvent. The uric acid residues were titrated with the same permanganate solution but the results were not calculated. There was no account taken of loss through washings and dilution, as exactly the same conditions prevailed in all three methods and any errors from that source were equal.

From a comparison of the results of these methods it will be noted that in our hands the hydrogen sulfide treatment was far superior to either of the others. The destructive action of the alkali was distinctly noticeable in both the sodium sulfide and ammonium sulfide treatments. These two checked very closely and the ammonia method gave slightly

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higher results than the sodium method but perhaps the higher results would not justify the extra difficulty involved.

TABLE VI.—0.2 GRAM SILVER MAGNESIUM URATE INVOLVED.

	H_2S method. Cc.	Na_2S method. Cc.	$(NH_4)_2.S$ method. Cc.
Cc. Standard $KMnO_4$ consumed	26.9	22.6	22.5
	27.0	22.7	22.8
	27.0	22.6	22.8
	27.0	22.6	22.7
	..	..	22.7[1]
	..	..	19.0[1]

The Influence of the Presence of Neutral Salts.—The Folin-Schaffer method for the determination of uric acid is based upon the fact that it is possible to precipitate uric acid as ammonium urate in the presence of ammonium sulfate without any loss of acid by the alkaline decomposition. The ammonium sulfate in the Folin-Schaffer reagent not only has a salting-out effect but it also prevents the destruction of uric acid.

Some time was given by the authors to an investigation of the action of piperazine on uric acid while various salts were present. The piperazine solutions were of the same strength as those used in the former experiments and consisted of 1 gram uric acid dissolved in a liter of water containing 3 grams piperazine. The piperazine was dissolved in about 400 cc. water and the weighed amount of uric acid was washed into this solution. At once the acid dissolved; the solutions were diluted to about 900 cc. in graduated liter flasks. The inorganic salts used were ammonium sulfate, disodium hydrogen phosphate and sodium chloride. Ten grams each of the above salts were carefully weighed and added to different piperazine urate solutions, only one neutral salt being allowed to be present in any one urate solution at a time. The resulting solutions were each diluted to the marks on the graduated flasks. On the addition of the ammonium sulfate the uric acid was largely thrown out of solution and on standing 24 hours still more uric acid had separated. The sodium monohydrogen phosphate did not completely dissolve and on standing 24 hours part of the material already in solution had separated from the solution. On the addition of the sodium chloride, solution was complete but after standing 24 hours an appreciable wart-like sediment had formed. Only one organic salt was used; this was lycetol, which is the tartrate of piperazine. The piperazine solution was prepared in the same way as the former ones and 5 grams lycetol were added. The latter dissolved practically completely. After 24 hours' standing, there was a slight separation of warty nodules.

Each solution of piperazine urate containing a neutral salt was allowed to stand 24 hours and then was filtered, the filtrate being preserved for

[1] The last two results were obtained with the use of CS_2 alone.

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future use. In order to determine how much uric acid did not go into solution, the residue and original flasks were washed with four small portions (25 cc. each) of cold water and then dissolved in about 500 cc. of boiling water. It was impossible to dissolve in 500 cc. hot water all the uric acid that had separated from the ammonium sulfate solution since the amount of uric acid involved was large. This residue however was washed into a beaker and dissolved with about 90 cc. concentrated sulfuric acid and this solution was added to the contents of the original flask. It was titrated with standard permanganate. The other three uric acid residues dissolved completely on the filter in hot water and these solutions were titrated at once after the addition of 75 cc. of concentrated sulfuric acid to each solution.

After two days' standing, samples of 100 cc. each were taken from each original filtrate that had been set aside previously. It was found that no further separation of solids had taken place except in the case of the sodium chloride solution, where it was necessary to filter again. To each of the samples taken, 15 grams solid ammonium sulfate and 5 cc. concentrated ammonium hydroxide were added. A heavy white precipitate was formed in each solution except in those samples taken from the ammonium sulfate solution. The various ammoniacal (NH_4OH) solutions were allowed to stand 24 hours when they were filtered and the residues were each washed with 100 cc. of 10 per cent. ammonium sulfate solution. The residues were then dissolved in about 200 cc. of hot water; after the addition of 30 cc. concentrated sulfuric acid to each solution, titrations were made with standard permanganate.

The same filtrate that furnished the two-day samples was also used to furnish samples after five more days' standing. These samples were taken and their uric acid content examined according to the directions just described. Still more uric acid had separated from the sodium chloride solution, so much that it was impossible to tell the exact uric acid content of the portion of solution involved.

TABLE VII.

	$(NH_4)_2SO_4$.	Na_2HPO_4.	NaCl	Lycetol.
Grams uric acid undissolved in 1000 cc.	1.0823	0.0164	0.0452	0.0148
Grams uric acid found per 100 cc. after two days	none	0.09248	0.09404	0.10028
(duplicates)	none	0.09248	0.09248	0.10068
Grams uric acid found after seven days. Per 100	none	0.0717	...	0.0846
cc. (duplicates)	none	0.0717	...	0.0839

At the outset 1 gram of uric acid had been placed in each of the piperazine solutions containing the respective neutral salts.

The results of this part of the work were not as satisfactory as we would have liked. It was very difficult to carry the work out quantitatively and the process itself depended on quantitative work to show

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the qualitative nature of the results. From the actual figures it would seem that we recovered in several cases more uric acid than we started with. We had no reason to doubt the factor on the permanganate solution used and it was not impossible that we have incorporated from the filtrations certain impurities that used up permanganate thus making our results, in terms of uric acid, run high. In any event, uric acid tended to separate from solution. Fairly concordant results were obtained for the uric acid content after two days. After seven days' standing, the results of the determinations showed a loss of uric acid and this information in itself was very desirable. Any error in the factor of the permanganate solution would have been uniform, for every effort was made to see that the respective uric acid solutions and residues were given the same treatment throughout the work, except where indicated. The presence of a salt did not entirely prevent the destruction of some uric acid in piperazine solutions. Ammonium sulfate seemed to completely salt out the uric acid; when once out of solution the piperazine seemed unable to act on the uric acid. Sodium chloride seemed to work in the same direction. Na_2HPO_4, NaCl and lycetol prevented the initial destruction of uric acid but with continued action, destruction of uric acid resulted to a quite marked extent.

Summary.

From the results of this work, it is quite evident that piperazine had a marked ability to dissolve uric acid in the cold. Urotropin, lycetol and ammonium hydroxide, although acting as bases, were poor uric acid solvents.

Piperazine, ammonium sulfide and ammonium hydroxide had marked destructive ability uricolytically, in the absence of neutral salts. Urotropin seemed to have but little effect on uric acid under the conditions employed. In the presence of certain neutral salts, decompositions of uric acid dissolved in piperazine were not so vigorous as in the absence of the salts. However, with continued action, there was a destruction of some of the uric acid.

In the boiling aqueous ammonium sulfide solution there seemed to be no reaction with uric acid to form thiouranil. Ammonium sulfide decomposed uric acid however to an extent nearly equal to that produced by sodium sulfide.

The work involved in this paper was done as partial fulfilment of the requirements in chemistry for the degree Master of Arts at Indiana University and this paper embodies the results of the investigation as presented in the thesis. The authors were particularly interested in any decompositions uric acid might suffer while using piperazine as a solvent, since piperazine is used so largely in medicine as a good uric acid solvent.

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The neutral salts selected were salts that would naturally be present in the living tissues.

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BLOOMINGTON, IND.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

AN ELECTRICALLY HEATED VACUUM FRACTIONATION APPARATUS.

BY H. S. BAILEY.

Received December 23, 1910.

In developing methods for the analysis of essential oils, it was found desirable to improve, if possible, upon the ordinary apparatus for fractional distillation *in vacuo* and, as a result of a year or more experimentation with various styles of apparatus, the following has finally been adopted.

The suggestion made by Richards,[1] that fractional distillations can be carried on much more expeditiously by the use of a heating coil within the distillation flask itself than when the heat is applied externally, led us to use a flask of the style shown in the accompanying sketch, A.

For working with 50 cc. portions of oil, this should have a capacity of approximately 150 cc. The heater B is a small coil of German silver or nichrome wire attached to platinum leads which in turn are sealed into the bottom of the flask. As it was desirable to distil off all but the last 10 per cent. (5 cc.) from the sample of oil and to leave as near as possible exactly this amount in the flask, it was necessary to have the bottom of the container as small as practicable. For this reason, it was made long and narrow, the 5 cc. mark being a little above the top of the heater. A fractionating head, C, of the Ladenberg type, is attached to the flask by a ground joint, the upper end of this head being extended some distance above the outlet tube so that the stopper through which

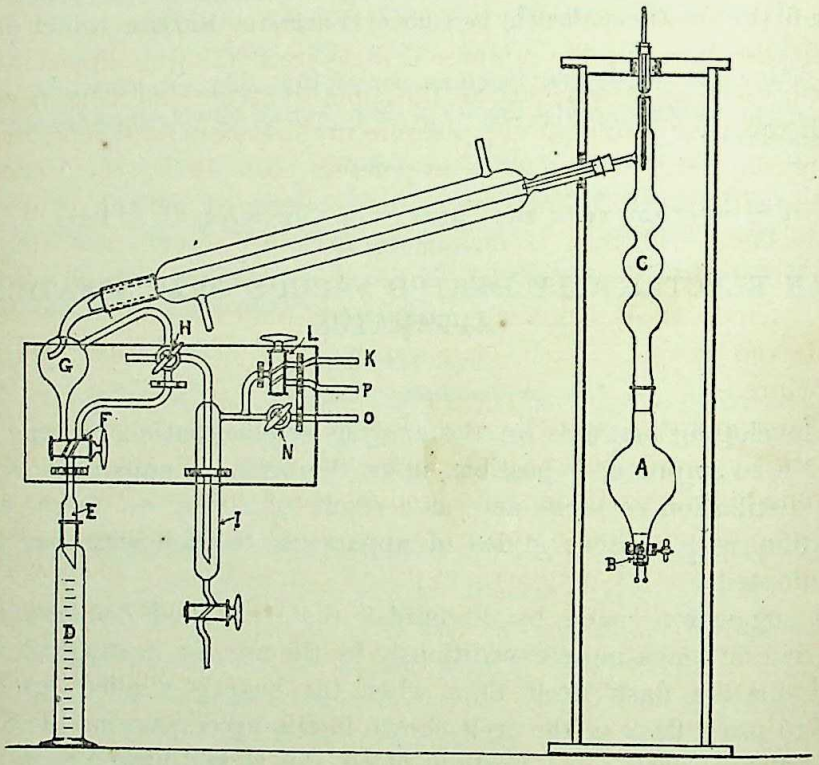
[1] THIS JOURNAL, 30, 1282; 31, 1200.

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the thermometer passes is in no danger of being attacked by hot vapors. The flask and head are enclosed in a wooden box to protect them from drafts as it was found otherwise impossible to carry on the distillation at a uniform rate.

The receiving end of the system is so constructed that either the distilling flask or the receiver may be evacuated, the one independently of the other. Thus, in beginning a distillation, the graduated cylinder D is slipped on to the ground joint E, stopcock F turned so as to connect this receiver with the safety bulb G and stopcock H which is a four-way cock bored with an L-shaped opening set so that the



safety bulb is connected with the evacuating system through a trap, I. This trap serves to catch any of the distillate which, in case of an accident, might otherwise be sucked through into the pump connections and lost. Tube K, attached to the house vacuum, is then connected with the system through stopcock L, and the major portion of the air in the entire apparatus quickly withdrawn. With the vacuum available in the Bureau of Chemistry, the pressure, as indicated on the manometer, will fall to about 20 mm. L is then closed and stopcock N, which is attached to an ordinary Chapman pump, opened, and by means of this the pressure still further reduced, in cold weather to about 12 mm. Cock N is then shut off, which, as it is a three-way, makes at the same

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time connection between the water pump and the outside atmosphere, preventing any backing up of the water, and L opened so as to connect I with the Geryk pump through the tube P. With this machine we are able to work readily below 5 mm. pressure. The current being turned on to the heater through a suitable rheostat, distillation is begun and the rate regulated as required by merely varying the external resistance.

When, for any reason, it is desired to separate one fraction from another, this is easily accomplished by reversing stopcock, F, thus closing G and connecting E directly with cock H, which may then be set so as to close the distillation system and open the receiver to the atmosphere. The first cylinder may now be removed and another one, which is ground to fit the taper of the adapter a little further down, slipped into place. Stopcock H is again turned, this time so as to connect the new receiver with the vacuum pump, the pressure in the boiling flask being unaffected. After the receiver has been evacuated, cock H is set to connect the pump with the distilling system and F reversed and the distillate which has collected in trap G during the exchange of cylinders, run into the new receiver. If proper precaution be taken to have all joints tight, the vacuum in the distilling flask and condenser will drop very little while the change of receivers is being made. Distillation then proceeds as before.

The apparatus, while it may look complicated, is in reality a comparatively simple one such as can be made up, with the exception of the distilling flask itself and the ground joints between the receivers and the adapter, in almost any laboratory from stock articles. The ground connections may be replaced by rubber if tube E be made with a long taper so as to fit into an ordinary graduated cylinder leaving just sufficient space for a rubber sleeve between the two.

It is not absolutely necessary that provision be made for connecting with the house vacuum and water pump previous to turning on the mechanical Geryk but this is desirable wherever practicable as it saves considerable time, and as a rule, oil immersion pumps work much better when they have only a small quantity of air to handle.

While there are no radical improvements in this apparatus over various others upon the market, still we have found that it combines the advantages of all of these without their disadvantages. In the method for separating fractions used by Brühl and others, it is impossible to work with one fraction until the distillation is complete or at least without interrupting it, but here as many fractions as desired may be taken off, one after the other, without changing the rate of distillation. This we have found to be very important where empirical methods are involved.

We have substituted in the heating coil other resistance materials

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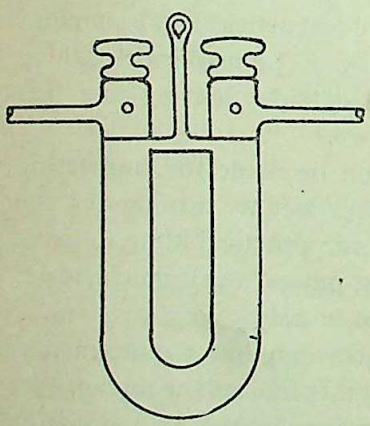
for platinum, not only as they are much less expensive, but also because with them the superheating and consequent bumping seems to be less. The joints between the heavy platinum leads used through the glass and the coil are made by twisting the two together and covering the union with a little bead of melted "Einschmeltz" glass. Probably because there is a high resistance at this junction, the bubbles of vapor originate here and rising through the body of the liquid keep it as well stirred as it would be with a stream of air. Of course, in working with liquids which would attack the base metals, the alloys cannot be used but they can safely be employed with most organic substances.

The fact that the source of heat is under absolute control makes it possible to regulate the rate of distillation very closely and to duplicate one's fractionations almost exactly. This is of great advantage where a number of samples of the same material are being examined, as often comparatively small variations in the rate of distillation materially affect the properties of the various fractions.

NOTE.

A Modified Drying Tube.—In view of the large percentage of breakage of U tubes and the resultant loss to the chemist of time and determinations when engaged in carbon analyses, the writer has endeavored to modify the usual form of tube in order to minimize this trouble.

In the accompanying photo is shown the tube as used in this laboratory and made for us by Eimer & Amend at an additional cost of only 25 cents each. The tube is of thick glass and is of the same bore throughout.



The brace and perpendicular bar are of glass possessing practically the same coefficient of expansion as the body of the tube, in order to properly withstand temperature changes, while the end of the upright bar is drawn into a loop, by means of which the tube may be suspended from the balance beam or train support. The advantage to be gained from this loop is great in having all the arm openings upon correct alignment during an analysis and in eliminating the use of wire in suspending.

Then, too, we do away with the changes of weight due to chemical action upon copper wire, which is usually used, and an entire glass surface is presented for wiping before weighing.

It can readily be seen that the breakage at the curve of the U, due of pressure or pull, is reduced to a minimum, and we believe the small

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additional cost of 25 cents each is more than equalized by the decreased breakage.

This tube has been in use for some time in this laboratory to our entire satisfaction, and we trust it may be of some value to other chemists who make an extensive use of drying tubes. W. H. McINTIRE.

STATE COLLEGE, PA.

NEW BOOKS.

Laboratory Experiments in General Chemistry. By HERMAN SCHLUNDT, Professor of Physical Chemistry, University of Missouri. 85 pages. Published by E. W. Stephens Co. Columbia, Mo. 1910. Price, 50 cents.

This small volume includes the more important experiments on the non-metallic elements as usually given in a course on General Chemistry. Experiments on the metallic elements have been omitted as the author feels "that this work should be undertaken in Analytical Chemistry, and be allotted some of the time so largely used for laboratory practice in following a scheme of separations." Careful and minute attention has been given throughout to all possible questions that may arise in the students' mind. The great amount of space required for this descriptive detail and instructive advice, literary as well as chemical, has precluded the consideration of many important subjects. Thus within the eighty-five pages, phosphorus and boron find no place and the sulfur, nitrogen, and silicon acids receive but little notice. The laboratory outline is well adapted for an elementary half-year course in first-year college chemistry. The student should find the explicit directions most helpful in laboratory and reference work. Cross-references are made to two texts: Alexander Smith's "General Chemistry for Colleges" and Kahlenberg's "Outlines of Chemistry." Chapter I on "Apparatus," and Chapter V on "Equivalent Weights," deserve especial mention for clearness and completeness of presentation. Unfortunately the drawings throughout the book are very poor. WILLIAM J. HALE.

Die Absorption. By J. M. VAN BEMMELEN. Published by Theo. Steinkopf, Dresden. 548 pp. 12 marks, unbound; 13½ marks, bound.

Those who know the literature of colloids, know also that Van Bemmelen is one of those rare experimenters who helped to lay the foundation of much of the recent work on colloidal hydrates and at a time when but a very few investigators were studying the subject. He is still active, though in his eightieth year, and Dr. Wo. Ostwald has now, with his assistance collected his separate publications which bear most directly upon the subject of colloids and particularly the subject of absorption. Dr. Jorissen has written a five-page biography of the author as an introduction to the work, as well as a complete bibliography of his publications.

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His exhaustive studies of the composition and stabilities of such substances as colloidal and precipitated ferric hydrate, silicic acid, stannic acid, etc., are here collected. He showed that this class of substances consists of the insoluble oxide with absorbed water, whose quantitative relationship to the oxide depends on the concentration of the water phase. His studies also covered the absorption of acids, salts, etc., from aqueous solutions by the colloidal precipitated oxides, and he found specific powers of absorption in some cases very marked. It seems as though each precipitate possesses, in conjunction with each different dissolved substance, a specific absorption tendency which varies both with the precipitate and with the soluble substance, and increases with increase of concentration of the solution.

The ratio between the concentration of the material absorbed and that held in the solution (absorption factor) is not a constant, as might be expected if partition of a solute between two solvents was considered as a criterion.

The applications of the researches of the author to agricultural and biological chemistry are given some attention and anyone reading the book cannot help being reminded of many practical applications of the principles described. The study of the gelatinous precipitates, commonly called insoluble hydrates, such as ferric hydrate, silicic acid, etc., are shown to be more properly, in most cases, insoluble oxides, whose water of constitution is entirely absorbed water and therefore generally not corresponding to any simple formula. The book makes a very satisfactory addition to the collected literature on colloids, as it presents the best experimental work done on that portion of the subject dealing with absorption.

W. R. WHITNEY.

A Text-Book of General Bacteriology. By WILLIAM DODGE FROST and EUGENE FRANKLIN MCCAMPBELL. MACMILLAN. New York, 1910. pp. 340 + XVII. Price $1.00 net.

In the preface to this volume the authors make the following statement: "There is no treatise in the English on the subject of general bacteriology except a translation of Fischer's 'Vorlesungen,' now more than a decade old. A brief but comprehensive text on this subject is a desideratum. The authors have attempted to meet this need in the present volume." The evident purpose to emphasize the value of bacteriology as a subject of general educational interest, and its claim to consideration as the subject in which the biological training of the student may be begun, is a worthy one, and in keeping with recent trend in biological education. It is certain that before bacteriology can take its place alongside zoölogy and botany as a subject introductory to real biological study, there will be need of text-books prepared with great care for this specific purpose. The present volume may well serve to

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impart an elementary idea of what bacteria are and of their most important activities, and will doubtless be useful as a text in a short, introductory course in bacteriology.

The introduction (13 pages) is a brief consideration of the history of the science and of the theory of spontaneous generation of life. Fifty-two pages are devoted to Morphology, thirty-six pages to Methods of Studying Bacteria, twenty-five pages to Taxonomy, fifty-six pages to General Physiology, ninety-eight pages to the Biology of Specialized Groups, and fifty-two pages to the Distribution of Bacteria, in which section the bacterial flora of various habitats are considered in relation to their environments. Fifty pages of the section on specialized groups are devoted to the pathogenic relations, and bacterial diseases, protozoal diseases, diseases of unknown causation, bacterial poisons, and immunity are here discussed. The treatment of the various subjects is general, in accordance with the title of the book. On the whole, the text gives the impression that the original sources of information have not been consulted to a great extent, and that the sources actually employed have not always been fortunately selected.

In many places the text is obscure and in some places erroneous, as might be expected in a first edition. The italicized statement, "It is not possible to cause any permanent change in the morphology of a bacterium and thus originate a new species of bacteria" (p. 25) may be a valuable one to emphasize to beginning students, but the same can hardly be said of the statement that the Brownian movement "is due entirely to the surface tension of the liquid medium in which the bacteria may be suspended" (p. 35), or that "Anthrax spores are the most resistant spores known" (p. 49), or that Dunham's solution "consists of a 10 per cent. peptone solution" (p. 71), or that vegetative bacteria cannot survive above 60° or below 0°, as might be gathered from the table on page 137, or that "This characteristic" (phosphorescence) "is common in various forms of life, particularly in marine animal forms among the photobacteria" (p. 170), or that group agglutinins "may be removed by diluting the serum" (p. 262). Such errors as "Schaudin" (p. 29), "tumeric" (p. 69), "media is neutralized" (p. 69), "Pasteur-Chamberlain" filter (p. 78), "Bacillus tetanus" (p. 98), and "spirilli" (p. 325), may be quickly imitated by students and the habit of using them is sometimes not easily overcome. The chemical symbols employed in the book will also require some attention in a subsequent edition. In the discussion of arthrospores on page 50, reference is made to Figure 38. This figure occurs on page 125 and represents a protozoan. On page 255 the use of the word "antitoxins" when endotoxins is meant leads to confusion in the treatment of this latter subject.

The book is printed in clear type on good paper, and is well bound.

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The illustrations are numerous and on the whole very good. Some of them, however, are not clear enough to convey anything to the mind of a beginning student and they should be replaced by better ones in subsequent editions. W. J. MACNEAL.

Elements of Crystallography. By W. S. BAYLEY, Ph.D. The McGraw-Hill Book Company. 236 pp., 300 illus. Price, $2.00 postpaid.

This book, offered "as a guide to those attempting to gain some insight into the fundamental principles of the science," is admirably printed, and well illustrated. It does not claim to be a guide to the practical study of crystals and cannot therefore be justly criticized for omissions noticed.

Considered as a simple elementary development or discussion of the science it is perhaps not unfair to point out that in two particulars at least Prof. Bayley's treatment suggests a "turning back of the hands of the clock." The general tendency for fifteen or twenty years has been to omit all tracing of the purely geometric relation between the forms of different symmetry, "holohedral" and "derived" or "partial" forms, as a needless piece of work since such forms are structurally different and can not both occur on crystals of the same substance. Similarly the reason for the preference given to the symbols of Naumann over those of Miller "because of the greater ease with which the Naumann symbols are comprehended by students who approach the study of crystals for the first time" is not in accordance with the experience of the writer. For the Weiss symbols this can be claimed but the abbreviated parameter symbols and the Miller indices lead equally quickly to the desired intercepts.

In the chapter (XII) on "crystal imperfections" Prof. Bayley presents concisely the usual variations from the ideal. Although so generally used the terms "imperfections," "distortions" and so on are not fairly correct designations, in most instances, but are attempts to set up an ideal for nature. For instance, following the general usage Prof. Bayley speaks of Fig. 208 as a "flattened octahedron" and of all such deviations from model forms as "not resembling the forms from which they were derived" whereas in fact there has been no such "derivation" and the crystal called an octahedron is simply a solid bounded by eight faces at 108° 29′ 16″ to each other. Millions of such occur but only rarely one that conforms to the added limitation that the faces must be equilateral triangles. The study of crystals has been made much more difficult by the conception of the "ideal form" which never occurs and is not in any way needed by the laws of crystals.

In the chapter on crystal aggregates Prof. Bayley does not succeed very well in attempted distinctions between "*crystal* aggregates" and "*crystalline* aggregates" and between crystal *individuals* and crystal *grains* as the following quotations show. The italics are not in the text.

"Rarely however are *crystal individuals* complete."

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"*Individual crystals* that exhibit only an occasional face"..... are distinguished as *crystal grains*."

"When the *grains* in an irregular aggregate are partially bounded by their own planes the aggregate is a *crystal aggregate*."

"Such aggregations as these where each grain is completely or almost completely bounded by other grains are distinguished as *crystalline aggregates*."

The chapter on crystal projection is brief and is principally the methods used for crystal drawing, clinographic projection and a little on linear projection. There is no description of projection as an aid to recognition of system and form but only as to methods of projection of determined forms.

The last fifty pages contain practically all that the space permits of the leading facts in physical and chemical crystallography.

To sum up. The writer disagrees with Prof. Bayley as to the better way of presenting the geometrical characters, but has however nothing but praise for the details of the presentation and for the admirable brief introductions to physical and chemical crystallography. A. J. MOSES.

"Salvarsan" or "606", its Chemistry, Pharmacy and Therapeutics. By W. HARRISON MARTINDALE, Ph.D., F.C.S., and W. WYNN WESTCOTT, M.B., D.P.H. New York: Paul B. Hoeber. 1911. 77 pages. $1.50 net.

Few remedies introduced in recent years have excited the interest shown in this widely advertized aromatic arsenic compound developed in the investigations of Paul Ehrlich, and known as salvarsan, which is the coined name for dihydroxy-diamino-arseno-benzene. The remedy was hailed as a specific in the treatment of syphilis, the scourge and curse of centuries, and anything of value here would naturally attract attention.

The little book by Martindale and Westcott contains in condensed form much of the matter which has appeared on the subject in the recent journal literature. It is a somewhat hasty compilation, and is not critically written. In fact, the whole style and aim of the book are not such as would allow it to be classed among scientific productions. But both sides of the controversy regarding the usefulness of the remedy are stated by the authors, and as pretty extended literature references are given the book will doubtless prove of value to a class of readers who wish to learn quickly the main facts in the case. J. H. LONG.

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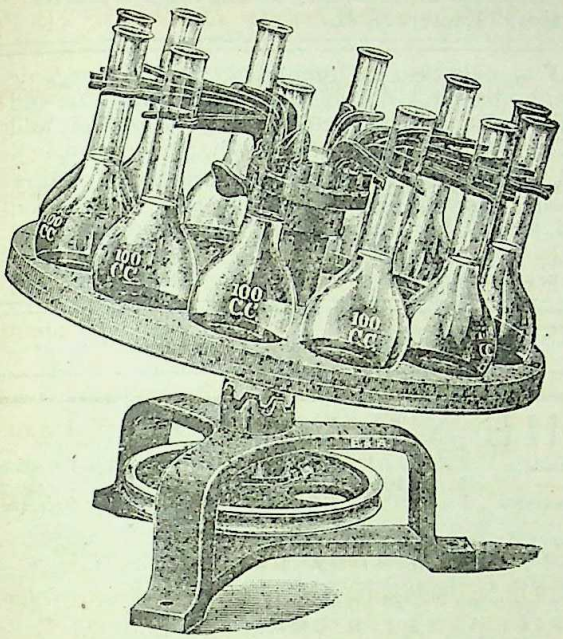
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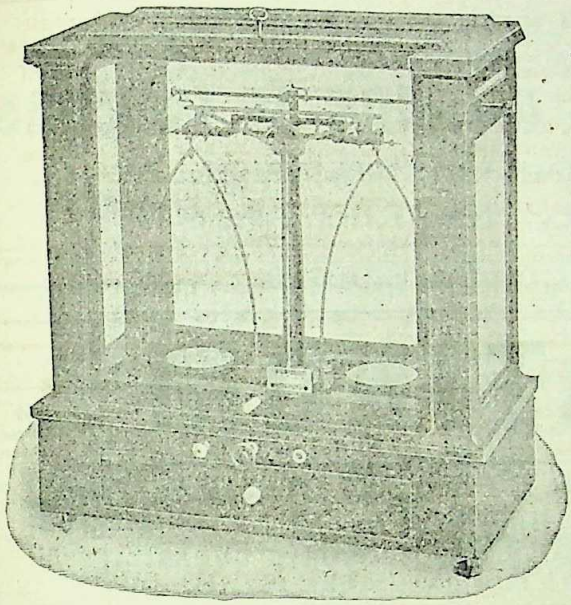
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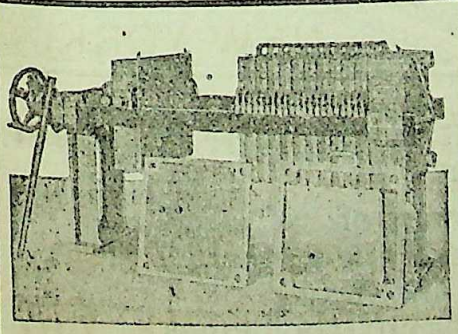
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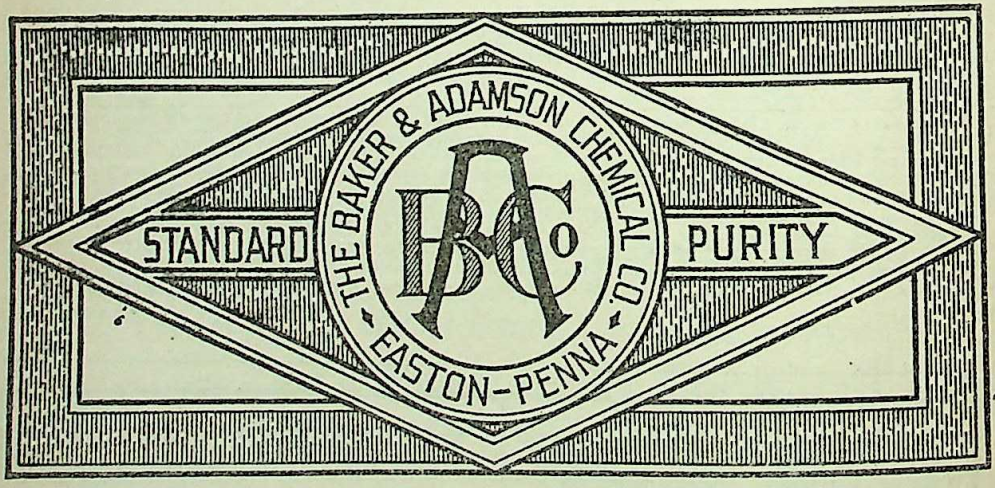
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Cellulose. The Cellulose Nitrates (Theory). Nitration of Cellulose (Practice). Cellulose Nitrate Solvents and Non-Solvents. Fusel Oil, Natural and Synthetic. Amyl Alcohols. Manufacture and Properties of Amyl Acetate, Natural, Artificial, Synthetic Camphor. Camphor Substitutes. Paint Removers. Turpentine Substitutes. Pyroxylin Solutions. Pyroxylin Lacquers. Bronzing Liquids. Waterproofing Compositions. Artificial Leather, Skin, Fur, Feathers, Rubber, Pyroxylin-Coated Leather and Splits. Patent and Enameled Leather. Celluloid, Pyralin, Xylonite, Viscoloid. Pyroxylin Plastics Celloidin and Cellulose Nitrates in Microscopy. Collodion and Cellulose Nitrates in Pharmacy, Medicine Film Manufacture and Photography. Artificial Silk, Whalebone, Gorse, Horsehair. The Cellulose Acetates. Guncotton and the Explosive Cellulose Nitrates. Viscose, Viscoid, and the Cellulose Xanthates. Denatured Ethyl Alcohol. Patent, Author, and Subject Index.

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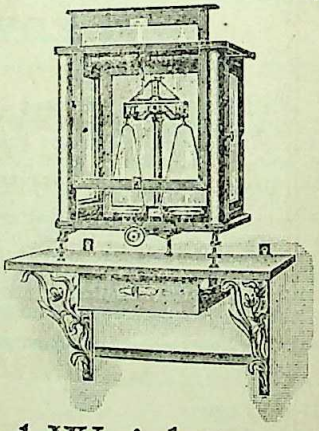
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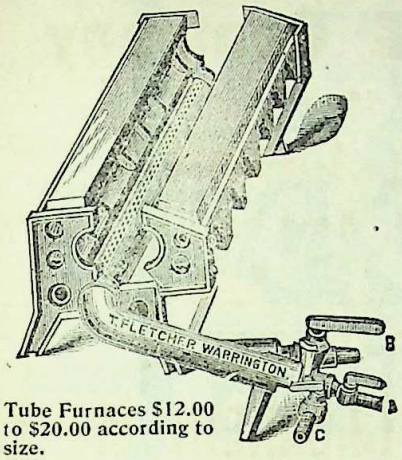
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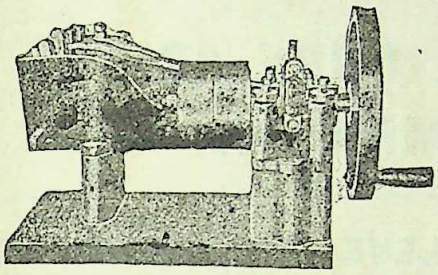
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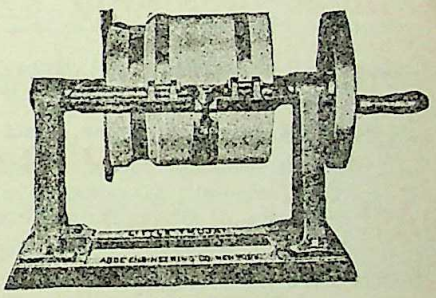
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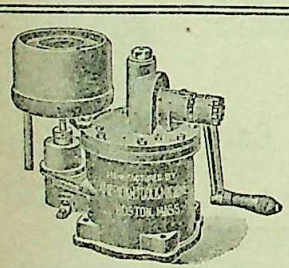
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MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

PUGET SOUND SECTION.

This Section held its regular annual meeting at the Faculty Club at the University of Washington on Saturday evening, Jan. 28th, and elected officers as follows: *Chairman* H. M. Loomis; *Vice Chairman*, A. Jacobson; *Secretary*, J. H. Linton; *Treasurer*, C. C. O'Loughlin; *Councilor*, H. G. Byers.

After the election a lunch was served, after which Mr. Walter P. Schuck gave a report of the winter meeting of the A. C. S., to which he had been appointed a substitute Councilor. J. H. LINTON, *Secretary*.

LOUISVILLE SECTION.

The regular monthly meeting was held February 13th, at the Galt House. Dinner was served at 6.30 P.M. An outline of the methods of determining fats, nitrogen, crude fiber and alcohol was given by Mr. A. M. Breckler, of the Sunny Brook Distillery. F. F. HASBROUCK, *Secretary*.

THE ST. LOUIS SECTION.

The February meeting was held in conjunction with the St. Louis Chemical Society at the Academy of Science, on the 14th.

Dr. F. W. Frerichs, President of the American Institute of Chemical Engineers, presented a paper on "Shipping Cylinders for Compressed and Liquefied Gases." This paper was illustrated with many diagrams, and specimens of various ammonia valves and cylinders.

R. NORRIS SHREVE, *Secretary*.

COLUMBUS SECTION.

A meeting of the Columbus Section was held Thursday, February 16th, at 8 P.M., in the Chemistry Building, Ohio State University. The topics for the evening were: Minor paper, "Points of View in the Teaching of Industrial Chemistry," by James R. Withrow. Major paper, "The Formation of Formaldehyde in the Vegetable Kingdom," by Professor Wm. McPherson. J. R. WITHROW, *Secretary*.

PHILADELPHIA SECTION.

The regular February meeting of the Section was held at the Engineers' Club, Philadelphia, on February 16th, after the usual dinner, at which the speaker of the evening, Dr. Bigelow, was present.

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The lecture of the evening was on "The Installation and Equipment of the Laboratory of the Bureau of Chemistry, United States Department of Agriculture," illustrated by numerous lantern slides, by Dr. W. D. Bigelow. Dr. Bigelow discussed the many novel features in this laboratory, which were found necessary for safety and convenience where many men are employed at a great variety of work.

C. S. BRINTON, *Secretary.*

LOUISIANA SECTION.

The forty-seventh regular meeting of the Section was held in the New Orleans Board of Trade Rooms, February 17th.

The paper of the evening was on "Recently Discovered Bacterial Decomposition of Sucrose," by W. L. Owen, bacteriologist at the Audubon Park Sugar Experiment Station. This paper was a summary of the result of two years' research, at the Experiment Station, on the bacterial deterioration of sugars.

GEORGE B. TAYLOR, *Secretary.*

MINNESOTA SECTION.

The regular meeting of the Section was held on Friday evening, February 17th, at 8 P.M., in the Chemical Laboratory of the University of Minnesota.

The following papers were presented: "Complete Electrolytic Dissociation in Saturated Solutions," by Ira H. Derby. "The Silver Salts of Tribromphenol," by William H. Hunter.

FRANCIS C. FRARY, *Secretary.*

KANSAS CITY SECTION.

The February meeting of the Section was held at the Y. M. C. A. Building, Kansas City, Mo., on Saturday evening, February 18th, beginning at five o'clock. The following papers were read: "Some Old Chemical Laboratories and their Apparatus," F. B. Dains. "The Effect of Nitrates on Drinking Water," C. C. Young. "A Photographic Copying Apparatus for Amateurs," A. V. H. Mory. Dinner was served at six-thirty.

E. A. WHITE, *Secretary.*

UNIVERSITY OF MICHIGAN SECTION.

The February meeting was held in Room 151, Chemical Building, Feb. 21st, with Prof. Gomberg in the chair, and an attendance of 24 members and numerous visitors. Papers were presented by E. H. Kraus on "An Improved Jolly Balance," and by A. H. White on "The Utilization of Coal." The executive committee was instructed to report to the Section at the March meeting, on the general question of Local Sections.

WILLIAM GABB SMEATON, *Secretary.*

THE UNIVERSITY OF ILLINOIS SECTION.

On Tuesday, February 21st, the Section held a joint meeting with the Illinois Water Supply Association. The following papers were presented: "Stoppage of Steam Pipes," by S. W. Parr. "New Method of Chemical

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Treatment of Water," by W. B. Bull. "Bacteriology of the Swimming Pool," by E. O. Jordan. "Notes on Treatment of Water for Boiler Use with Barium Hydrate," by G. N. Prentiss.

On Tuesday, February 28th, Dr. T. B. Wagner, of the Corn Products Company, gave an address on "The Industry of Corn Products," illustrated by lantern slides and samples of the products.

GRINNELL JONES, *Secretary.*

MILWAUKEE SECTION.

A regular meeting of the Section was held on Friday evening, February 24th, at the Hotel Blatz. The address of the evening was by Dr. Lee F. Hawley, of the U. S. Forest Products Laboratory, on "Some Chemical Methods of Utilizing Waste Wood." The various processes of distilling wood and the resulting products were thoroughly discussed and some phases of the paper-making industry were taken up.

BEN L. SALOMON, *Secretary.*

SECTION OF WESTERN NEW YORK.

A general meeting was held at the University, High Street, Buffalo, on February 28th, at 8.15 P. M. The following papers were read: "Some Blood Tests," by Dr. G. H. A. Clowes. "Alundum Laboratory Appliances," by Mr. L. E. Saunders. An informal dinner at the German American Hotel preceded the meeting.

WALTER WALLACE, *Secretary.*

CLEVELAND SECTION.

The March meeting was held in the auditorium of the National Carbon Company's Cleveland Plant, Monday evening, March 6th.

Before the regular program, the members were shown through the Company's laboratories and rooms where the routine tests are made on dry cells, arc lamp carbons and other carbon products.

Mr. W. R. Hulbert, sales manager of the Goldschmidt Thermit Company, gave an interesting talk on thermit, its properties and uses. Mr. Hulbert showed some excellent slides illustrating the various applications of thermit in repairing large and small castings. At the end of his talk, the lecturer gave a practical demonstration of several types of welding operations.

About two hundred members and guests were present. After the meeting adjourned, a complimentary lunch was served by the National Carbon Company.

W. R. VEASEY, *Secretary.*

CINCINNATI SECTION.

The one hundred and sixty-seventh regular meeting of the Section was held on Wednesday evening, March 8th, at the Ohio Mechanics Institute. The following papers were presented: "The Determination of the Hardness of Water," by Clarence Bahlman. "The Filtration Plant of the City of Washington," by Dr. Folsom.

ALFRED SMITH, *Secretary.*

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WASHINGTON SECTION.

The two hundred and fifth meeting was held at the Cosmos Club, Thursday, March 9th, at 8 P.M. The program was as follows: "The Density and Thermal Expansion of Anhydrous Ethyl Alcohol and of its Mixtures with Water," N. S. Osborne, E. C. McKelvy and H. W. Bearce. "Physical Relations," H. W. Bearce. "Chemical Aspects," E. C. McKelvy. "Studies on the Thermal Death Point of Milk Enzymes," W. N. Berg. "Potash from Feldspar," Bernard Herstein.

H. S. BAILEY, *Secretary.*

NEW YORK SECTION.

The sixth regular meeting of the session of 1910–'11 was held at the Chemists' Club, on March 10th.

The election of officers for the session of 1911–'12 resulted as follows: *Chairman*, A. C. Langmuir; *Vice-Chairman*, A. B. Lamb; *Secretary and Treasurer*, C. M. Joyce; *Executive Committee*, Chas. Baskerville, David Wesson, W. J. Evans, Rudolph Seldner.

The following papers were presented: "The Sulfides of Iron," by E. T. Allen. "The Detection of Salicylic Acid," by H. C. Sherman and A. Gross. "A Study of the Factors Involved in the Qualitative Determination of Barium," E. Frankel and L. J. Curtman. "The Detection of the Platinum Metals by the Glow Reaction," by P. Rothberg and L. J. Curtman. "Some New Rare Earth Compounds," by Charles James. "Experimental Furnaces for Glass Melts," by P. C. McIlhiney. "Examination of Commercial Oxygen," by Reston Stevenson and Chas. Baskerville.

Before the reading of the last paper, the Chairman asked Dr. Sabin, the first Chairman of the Section, to preside. Dr. Sabin, in taking the chair, gave a short account of the early history of the Section. Dr. McMurtrie had hoped to be present to make some valedictory remarks on the occasion of the last meeting in the old quarters of the Chemists' Club, but was obliged to send a written communication instead, which was read by Prof. Baskerville.

C. M. JOYCE, *Secretary.*

EASTERN NEW YORK SECTION.

The regular meeting for March was held in the Chemical Laboratory of Union College, Schenectady, on Friday evening, March 10th, at 8 o'clock. The address of the evening was "A Universal Law," by Prof. Wilder D. Bancroft.

G. R. FONDA, *Secretary.*

DECEASED MEMBERS.

Harrison Everett Ashley, Pittsburg, Pa.
Emile Maertens, Providence, R. I.
J. H. van't Hoff, Charlottenburg, Germany.

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VOL. XXXIII. APRIL, 1911. NO. 4.

THE JOURNAL

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American Chemical Society

ON THE FORMATION OF DOUBLE SALTS.

[SECOND PAPER.]

THE DOUBLE CAESIUM MERCURIC CHLORIDES FORMING FROM ACETONE.

BY H. W. FOOTE AND F. L. HAIGH.

Received January 26, 1911.

In a previous article,[1] we considered the effect of a change in solvent on the formation of double salts which yield hydrates when crystallized from water. It was shown that the substitution of alcohol or acetone for water as solvent may produce salts of an entirely different type from those crystallizing from water, or may entirely prevent the formation of a double salt. Thus, there are three hydrated potassium mercuric chlorides which form, at 25°, from water while there is but one double salt formed from alcohol and two from acetone and all are different in type from the hydrates. The conclusion was drawn that when a double salt is formed containing the solvent, the latter is an essential constituent of the salt and is as important in determining the type of double salt formed as are the individual salts.

The case appears to be very different when double salts are formed which do not combine with the solvent. In general, it is to be expected that two single salts capable of forming an anhydrous double salt from one solvent should form the same salt from any other solvent unless the latter also enters into the compound. This can be demonstrated theoretically in a number of ways. If, for instance, the reverse is assumed, that a double salt AB forms from one solvent, while the single salts A and B are deposited by another, then the salt AB could be brought into contact with the second solvent in equilibrium with the single salts, and it would decompose into A and B. The latter could then be brought into contact with the first solvent in equilibrium with double salt and

[1] THIS JOURNAL, 32, 618 (1910).

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would form double salt, thus bringing about a perpetual motion. We have tested this conclusion in the present investigation by determining experimentally the double salts formed from a non-aqueous solution and comparing them with the anhydrous salts forming from water.

An unusual series of such anhydrous double salts is formed from water by caesium and mercuric chlorides. They were first described by Wells[1] and were again investigated by one of us[2] by the solubility method. They have the following formulas: $CsCl.5HgCl_2$, $CsCl.2HgCl_2$, $CsCl.HgCl_2$, $2CsCl.HgCl_2$, $3CsCl.HgCl_2$. We chose this series for investigation partly because one component, at least, mercuric chloride, is readily soluble in many organic solvents and partly because the series is the longest of any we know.

The same solubility method was applied which was previously used in investigating these salts. Absolute alcohol was first tried as a solvent. Double salts formed without question, as was shown by variable solubility, but the time required to reach equilibrium was too great, due to the low solubility of caesium chloride, and conflicting results were obtained. We then tried acetone. The salts were ground in a mortar and the solubility of mixtures determined. Here, again, we met with difficulty as equilibrium was reached very slowly and the results were irregular. The solubilities were, in general, greater than where alcohol was used, however, and the method appeared practicable, if the original caesium chloride were sufficiently fine. In all subsequent work, this salt was first ground and then sifted through the finest silk bolting cloth we could obtain. Mercuric chloride offered no special difficulty in reaching equilibrium as it is very soluble and it was accordingly ground in a mortar and not sifted. Weighed quantities of the salts, in varying proportions, were placed in glass-stoppered bottles and a measured volume of acetone added from a pipet. The mixtures were at once shaken vigorously to prevent lumps from forming, the bottles were sealed with paraffin and rotated in a thermostat at 25°. All mixtures were shaken at this temperature for at least forty-eight hours. A sample of the solution was then removed through a filter of glass wool into a weighed specimen tube for analysis. The residues were dried as rapidly as possible on filter papers. They were somewhat contaminated with salts from the solutions as the solvent is very volatil, and the analyses, in consequence, show a somewhat high percentage of mercuric chloride. Mercury was determined in both solution and residue by precipitating as sulfide, filtering on a Gooch crucible and drying at 110–120°. In the case of solutions, the filtrate from mercuric sulfide was evaporated to dryness and caesium weighed as chloride. In analyzing residues, caesium chloride

[1] *Am. J. Sci.*, 44, 221 (1892).
[2] *Am. Chem. J.*, 30, 339 (1903).

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was determined by difference, as tests in a closed tube showed in every case that there was no solvent of crystallization.

The results obtained, using sifted caesium chloride, are given below in the table. One result only, of all that were obtained on sifted material, is not given, as it was obviously in error.

SOLUBILITY OF CAESIUM AND MERCURIC CHLORIDES IN ACETONE AT 25°.

No.	Per cent. $HgCl_2$ in solution.	Per cent. CsCl in solution.	Per cent. $HgCl_2$ in residue.	Residue contains.
1	57.74	0	100	$HgCl_2$
2	57.79	0.13	98.91	$HgCl_2$ and $CsCl.5HgCl_2$
3	57.74	0.14	95.98	
4	57.74	0.20	89.16	$CsCl.5HgCl_2$
5	52.54	0.22	89.36	
6	49.83	0.32	89.32	
	Calculated for $CsCl.5HgCl_2$		88.94	
7	44.32	0.50	87.35	$CsCl.5HgCl_2$ and $CsCl.2HgCl_2$
8	44.46	0.44	79.90	
9	39.65	0.48	77.30	$CsCl.2HgCl_2$
10	28.48	0.48	76.99	
	Calculated for $CsCl.2HgCl_2$		76.29	
11	26.96	0.52	72.63	$CsCl.2HgCl_2$ and $CsCl.HgCl_2$
12	27.32	0.61	63.48	
13	21.50	0.46	62.15	$CsCl.HgCl_2$
14	13.08	0.45	62.24	
	Calculated for $CsCl.HgCl_2$		61.67	
15	0.16	0.19	54.02	Mixtures of several salts
16	0.17	0.25	37.88	
17	0.02	0.11	18.17	
18	0	0.032	0	CsCl

In the table, Nos. 1 and 18, respectively, show the solubility of pure mercuric chloride and caesium chloride. Excluding Nos. 15–17 for the time, the results are grouped, each group representing (1) constant solubility and varying residue where a mixture of two salts was present or (2) varying solubility and constant residue showing a pure salt. The relation of the solutions to each other is better shown by the mercuric chloride than by caesium chloride as the latter is so small in every case that the errors of analysis hide the regularities. It is evident from the results that three, at least, of the five salts which form from water also form from acetone. The residues in Nos. 15–17 correspond respectively in composition to mixtures of the 1 : 1 and 2 : 1, the 2 : 1 and 3 · 1 and

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the 3 : 1 and caesium chloride. The solubilities in these cases are exceedingly small and no conclusions can be drawn from them as to what salts were present in the mixtures. We were therefore forced to rely on microscopic examination of the residues to determin what salts were present.

The crystals of all the caesium mercuric chlorides have been investigated by Penfield,[1] so that his descriptions were available for comparison. We also prepared the pure 2 : 1 and 3 : 1 salts from water. The proportions of salts and water used in preparing these double salts were calculated from solubility results obtained in a previous article.[2] The solutions were cooled rapidly to form small crystals for comparison with the small crystals obtained from acetone. Finally, duplicates of Nos. 15–17 were prepared as before, shaken at 25° for three days and then allowed to rest for several days, the object being to obtain as well-formed crystals as possible. Shaking in the thermostat injures the crystals but is necessary in order to make the salts form. Standing at rest sharpened the crystal forms considerably. The 3 : 1 salt prepared from water showed crystals of the form figured by Penfield, slender crystals with unsymmetrical terminations. The 2 : 1 salt was not figured by Penfield but our specimen showed flat plates with characteristic cleavage at right angles. Both salts are birefringent. From acetone, No. 17 showed the best crystals. In this, there were three perfectly distinct substances, (1) rounded masses of isotropic material, evidently caesium chloride, (2) crystals identical in appearance with the 3 : 1 salt with characteristic unsymmetrical terminations, and (3) flat plates like the 2 : 1 salt prepared by us and described by Penfield. There could be no question of identity of the two anisotropic substances with the 2 : 1 and 3 : 1 double salts from water. Nos. 15 and 16 showed similar crystals of these two double salts and also more or less of the 1 : 1 salt. The latter is isotropic like caesium chloride so that it could be readily distinguished under crossed Nicols from the other forms. No indication of salts other than those mentioned was obtained. Of course a system containing three salts, as in No. 17, is unstable and one salt should disappear. The slight solubility of the salts, however, makes it a difficult matter to reach complete equilibrium.

We consider the evidence complete that from water, acetone, or in general from any solvent, the same anhydrous double salts are formed.

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[1] *Am. J. Sci.*, [3] 44, 311 (1892).

[2] *Loc. cit.*

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ON THE FORMATION OF DOUBLE SALTS.

[THIRD PAPER.]

THE QUESTION OF DOUBLE SALT FORMATION BETWEEN THE ALKALI SULFATES.

By H. W. Foote.

Received January 26, 1911.

I. Sodium and Potassium Sulfates.

Sodium and potassium sulfates when crystallized together from solution yield homogeneous crystals containing both sodium and potassium. The question as to what these crystals are—whether a double salt or an isomorphous mixture of single salts—has been the subject of a surprising number of investigations which have yielded very contradictory results.

The older literature on this subject is well summarized by Retgers,[1] who mentions at least twelve investigations. In the older work, various formulas were proposed for the crystals varying from $5K_2SO_4.Na_2SO_4$ to $4K_2SO_4.3Na_2SO_4$. Retgers, starting on the assumption that mixed crystals were formed and not a double salt, demonstrated first that there was not a complete series of mixed crystals, but that pure potassium sulfate may form, mixed mechanically with crystals containing a considerable proportion of sodium sulfate. He determined the specific gravity of crystals containing both sodium and potassium and found it higher than either of the single salts instead of being intermediate and concluded from this fact that a compound must be present and not mixed crystals. By fractioning his material with a heavy solution and choosing the heaviest crystals for analysis, he reached the conclusion that the substance had the composition $3K_2SO_4.Na_2SO_4$. Some time afterward, Bandrowski[2] assigned the formula $2K_2SO_4.Na_2SO_4$ to the crystals and Kubierschky[3] obtained crystals from a hot solution corresponding in composition also to the 2 : 1 salt. van't Hoff and Barschall,[4] by crystallization experiments at different temperatures, obtained crystals varying widely in composition and assumed that no compound was present, but that there was merely a limited series of mixed crystals varying in composition between 78 and 61 per cent. of potassium sulfate. The following year, Gossner,[5] working in Groth's laboratory and aware of the work of van't Hoff and Barschall, investigated several samples of the sulfates prepared from solutions which varied greatly in composition and concluded that only the 3 : 1 compound formed and that mixed crystals

[1] *Z. physik. Chem.*, 6, 205 (1890).
[2] *Ibid.*, 17, 234 (1895).
[3] *Sitzb. kgl. preuss. Akad. Wiss.*, 1902, 413.
[4] *Ibid.*, 1903, 359.
[5] *Z. Kryst. Min.*, 39, 155 (1904).

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were not present. Finally, van't Hoff and Barschall[1] again asserted the formation of mixed crystals in opposition to the work of Gossner. It will be seen from the above review that while the majority of investigators concluded that double salts formed, nevertheless, there is good ground for assuming mixed crystals, due particularly to the work of van't Hoff and Barschall.

It has seemed to us that the problem could be settled by a method which has been used before in a considerable number of cases for determining double salts. The method consists in treating a series of mixtures of the salts with water and after thorough shaking, determining the composition of the solution and residue. Two or more mixtures having constant solubility and varying residue indicate a mechanical mixture of two substances. Varying solubility and constant composition indicate a pure double salt while varying solubility and varying composition in a series show that mixed crystals are present instead of a double salt.

The method outlined involves a considerable number of analyses and for the present purpose it was necessary that they should have a considerable degree of accuracy. Most of the previous investigators have analyzed their products merely by determining sulfate with barium chloride. This indirect method involves considerable error. The method using hydrochloroplatinic acid is much more accurate and has been used in a very few cases but as ordinarily carried out it involves converting the alkali sulfates to chlorides, which requires much time. The Lindo-Gladding modification of the method is much more rapid and very accurate as we have convinced ourselves by experiment. By this method, the sulfates are evaporated directly with the platinum solution, treated with 80 per cent. alcohol, filtered on a Gooch crucible and washed. This leaves much sodium sulfate insoluble in the alcohol. The residue is then washed with a 20 per cent. solution of ammonium chloride, saturated with potassium platinic chloride, to remove sodium sulfate, and again with 80 per cent. alcohol, after which the potassium salt is dried and weighed as usual. We have used this method throughout the work.

In the first series of experiments, varying mixtures of anhydrous sodium sulfate and potassium sulfate were treated with water in small bottles. They were heated in a bath of boiling water for some time, then cooled and shaken in a thermostat at 25° for from forty-eight hours to a week. For analysis, the solution was removed through a filter of glass wool and the residue was dried between filter paper. The salts were always very granular and they could be dried in this way very rapidly with the certainty that the impurity introduced from the solution was very small. We preferred this method to washing with water and alcohol, which has

[1] *Z. physik. Chem.*, 56, 212 (1906).

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sometimes been used, as the water might dissolve the single salts unequally from the crystals. van't Hoff mentions that when the latter are moistened with water, a deposit of pure potassium sulfate forms.

The results obtained in the first series were as follows:

TABLE I.—SOLUBILITY OF MIXTURES OF SODIUM AND POTASSIUM SULFATES AT 25°.

No.	Per cent. K_2SO_4 in solution	Per cent. Na_2SO_4 in solution.	Per cent. K_2SO_4 in residue.	Remarks.
1.....	10.93	5.72	88.97	Mixtures.
2.....	10.82	5.78	84.84	
3.....	9.71	8.22	78.16	Original K_2SO_4 not all dissolved in hot solution.
4.....	7.98	13.94	77.31	Original K_2SO_4 not all dissolved in hot solution.
5.....	7.53	15.92	77.40	Original K_2SO_4 not all dissolved in hot solution.
6.....	7.47	16.80	74.67	Original Na_2SO_4 not all dissolved in hot solution.
7.....	6.89	19.56	75.32	Both salts dissolved in hot solution.
8.....	6.59	21.28	74.91	Both salts dissolved in hot solution.
9.....	6.08	23.74	74.37	Solution slightly supersaturated with respect to $Na_2SO_4.10H_2O$.
10.....	6.33	22.56	24.86	Mixtures containing $Na_2SO_4.10H_2O$.
11.....	6.24	22.68	8.12	

The results given above are unsatisfactory in some respects, but they show certain things and are given for what they are worth. First, they show clearly the limits outside of which mixtures are formed for in Nos. 1 and 2 and 10 and 11, the solubility results are constant, while the residues vary. Nos. 3–9 show variable solubility, indicating but one phase present in each case instead of two but the residues are not constant in composition as a double salt would be, nor do they vary regularly with the composition of the solution, as mixed crystals should do. There is, however, a difference of nearly four per cent. in the composition of the residues, which is much greater than could be accounted for by impurities adhering from the solution, and indicates that the residues are variable in composition, due to the formation of mixed crystals. The irregular variation is pretty certainly due to equilibrium not being completely reached in the crystals. In No. 6, the presence of solid sodium sulfate in the residue at first would tend to form mixed crystals with the maximum amount of that salt present and when once formed, the slight change of composition necessary for equilibrium with the solution would require a long time. The same may be said of Nos. 3–5 with regard to potassium sulfate.

In the second series of experiments, calculated mixtures of the single salts and water were used in such proportions that all salts should be dis-

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solved when hot and crystallize a small amount of the single phase on cooling. The mixtures were shaken as before at 25°. The results are given in Table II.

TABLE II.

No.	Per cent. K_2SO_4. in solution.	Per cent. Na_2SO_4 in solution.	Per cent. K_2SO_4 in residue.
A	9.06	10.14	77.24
B	8.04	14.16	76.64
C	6.91	19.40	75.22
D	6.52	21.17	75.86

Comparing the solubilities in Table II with those in Table I, it will be seen that all four are within the limits which yield a single solid. The residues were granular and on this account could be freed very easily indeed from the mother liquor. Their difference in composition cannot be due to impurities from solution but to the formation of mixed crystals. The fact that the residue of *D* contains somewhat more potassium sulfate than that of *C*, is undoubtedly due to the fact that perfect equilibrium is established very slowly in the solid.

For the third series, two mixtures were prepared using such proportions of salts and water that a single solid in small amount should be formed from solutions which were very near opposit limits. The amounts used were:

	K_2SO_4. Grams.	Na_2SO_4. Grams.	H_2O. cc.
I	17.	14.	125
II	14.	40.	125

The salts and water were warmed till all dissolved and then allowed to cool in the thermostat without shaking. After several days, the small crops of crystals were removed and analyzed. The solutions were not analyzed, but from the original proportions used, would have approximately the composition given in Table III. The residues were analyzed in duplicate.

TABLE III.

No.	Per cent. K_2SO_4 in solution (approximate).	Per cent. Na_2SO_4 in solution (approximate).	Per cent. K_2SO_4 in residue.	
I	9.7	8.2	78.08	77.80
II	6.5	21.2	74.38	74.33

The difference in composition of the residues is about 3.5 per cent. which shows again that the residue is variable in composition or in other words, that a limited series of mixed crystals is present and not a double salt. This conclusion confirms the work of van't Hoff and Barschall.

The limiting composition of this series of mixed crystals at 25° can be approximately calculated. Taking the results in Table III as being nearly correct and assuming that the residue changes as a linear function

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of the percentage of sodium sulfate in solution, the limiting values at 25° would be about 78.6 per cent. and 73.9 per cent. of potassium sulfate. These values for 25° probably are very near the truth but the limits doubtless change with the temperature as van't Hoff and Barschall have indicated.

II. Sodium and Caesium Sulfates.

In connection with the foregoing work on potassium and sodium sulfates, we have determined the solubility of mixtures of sodium and caesium sulfates, as this case has an indirect bearing on the previous one. Caesium in its compounds does not resemble sodium even as closely as potassium does while it has a greater tendency than potassium to form double salts. If the preceding sodium potassium sulfate had been a double salt, therefore, it would be expected that caesium would form one or more also, while if mixed crystals formed in the previous case, caesium would less likely be isomorphous with sodium and the two sulfates should crystallize side by side without forming mixed crystals.

Pure caesium sulfate was prepared by evaporating a solution of the chloride with a slight excess of sulfuric acid. The residue was heated in platinum to be sure chlorides were removed, then dissolved in water and barium hydroxide added in the presence of phenolphthalein till the solution was neutral. Barium sulfate was removed by filtering and the solution evaporated to dryness. The salt is exceedingly soluble. This method of preparing the normal sulfate in considerable quantity is much easier than the method of igniting the acid sulfate with ammonium carbonate or in a current of ammonia.

Mixtures of the two sulfates and water were prepared as before and shaken at 25°. The determination of caesium was carried out exactly like the potassium determination previously described, a solution of ammonium chloride being used which was saturated with caesium chloroplatinate.

The following results were obtained:

No.	Per cent. Cs_2SO_4 in solution.	Per cent. Na_2SO_4 in solution.	Per cent. Cs_2SO_4 in residue.	Empirical composition of residue.
1.....	54.65	11.44	89.98	$1Na_2SO_4.3.53Cs_2SO_4$
2.....	54.58	11.63	78.22	$1Na_2SO_4.1.41Cs_2SO_4$
3.....	54.81	11.25	34.67	$4.8Na_2SO_4.Cs_2SO_4$

The composition of the solution remains constant while the composition of the residue varies between wide limits. This shows that neither double salts form nor mixed crystals analogous to those of sodium and potassium sulfates.

It may be added that all the caesium-sodium residues contained no water showing that sodium sulfate crystallizes anhydrous at this temperature in the presence of so much dissolved salt. The decahydrate formed, however, in mixtures No. 10 and 11 of Table I, where mixed crystals of

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sodium and potassium sulfate were mixed mechanically with sodium sulfate.

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

EQUILIBRIUM BETWEEN ALKALI-EARTH CARBONATES, CARBON DIOXIDE AND WATER.

BY HERBERT N. MCCOY AND HERBERT J. SMITH.

Received January 25, 1911.

In view of the importance of an accurate knowledge of the state of equilibrium between calcium carbonate, carbon dioxide and water and the fact that previous experimenters[1] had not used modern physico-chemical methods, nor carried the measurements to higher pressures than 6 atmospheres, we undertook a study of the system in question.

As is well known, the concentration of dissolved lime increases with increasing concentration of carbonic acid. The theory of the equilibrium has been treated by van't Hoff,[2] Bodländer[3] and Stieglitz.[4]

The following fundamental equations govern the equilibrium:

(1) $$H \times HCO_3 = k_1 \times H_2CO_3.$$

(2) $$H \times CO_3 = k_2 \times HCO_3.$$

(3) $$Ca \times CO_3 = k_3,$$ the solubility product.

(4) $$HCO_3 = 2Ca.$$

(5) $$Ca = \alpha \times Ca(CHO_3)_2.$$

If k is the equilibrium constant for reaction,

(6) $$\frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}} = \sqrt[3]{\frac{k_1 k_3}{4 k_2}} = k.$$

Bodländer showed that Schloessing's experiments gave a good equilibrium constant and calculated k_3, the solubility product of calcium carbonate, from the results. The value found is erroneous[5] owing to the use of an incorrect value for the secondary ionization constant of carbonic acid. Stieglitz has made a critical recalculation of the solubility product from Schloessing's experiments and other available data giving k_1 and k_2. Seyler and Lloyd[6] have also studied the problem under conditions applicable to geological problems.

In our experiments, for partial pressures of carbon dioxide, less than

[1] Schloesing, *Compt. rend.*, 74, 1552; 75, 70 (1872); Engler, *Ann. chim. phys.*, [6] 13, 348 (1888). Seyler and Lloyd, *J. Chem. Soc.*, 95, 1347 (1909).

[2] *Z. physik. Chem.*, 1, 505 (1887).

[3] *Ibid.*, 35, 23 (1900).

[4] *Carnegie Inst. Publication*, 107, 233 (1908).

[5] Stieglitz, *Loc. cit.* McCoy, *Am. Chem. J.*, 29, 437 (1903.)

[6] *Loc. cit.*

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one atmosphere, 500 cc. glass bottles were used. For higher pressures we used a 2 liter seamless, pressed steel bottle with a needle valve, capable of withstanding the pressure of liquid carbon dioxide. The inside of the bottle was effectively protected from the action of the carbonic acid by a thin coating of a mixture of beeswax and Venice turpentine, applied hot. The calcium carbonate used was made by precipitating pure calcium nitrate with ammonium carbonate at 15° and washing the precipitate free from ammonium nitrate. By working in the cold the calcite variety was obtained.

The glass bottles were charged with about 50 g. of calcium carbonate and 250 cc. of water; the steel bottle with about double these quantities. Carbon dioxide was then introduced in the desired amount. For experiments at greater than atmospheric pressure the gas was drawn from a steel cylinder of liquid carbon dioxide. The charged bottles were rotated in a thermostat at 25° + 0.02 for from 2 to 3 days, in which time equilibrium was reached. At low pressures the bottles were allowed to stand in the thermostat until the solution became clear. Portions of the latter were then removed by a pipet and analyzed. For high pressures, a brass tube, 1 × 5 cm., filled with cotton and attached to the inside of the needle valve of the steel bottle, served to filter the solution. Suitable portions of the filtered solution were drawn off into tared, evacuated, round-bottomed flasks. For the carbon dioxide analysis, the flask contained a solution of barium chloride and a known volume of standard potassium hydroxide, so that, although the carbonate solution gave off gaseous carbon dioxide as soon as the pressure was released, none of the gas was lost. The amount of solution taken for analysis was determined by weight and the excess of alkali titrated with 0.05 *N* hydrochloric acid, using phenolphthalein as indicator.[1] In the analysis for calcium the solution was run into a dry flask and although it became supersaturated with $CaCO_3$, owing to loss of CO_2, it remained clear for a sufficient time to prevent deposition of $CaCO_3$ in the valve or connecting tube. The solution was weighed and then titrated with *N*/20 HCl, using methyl orange as indicator.

The results of the experiments are shown in the accompanying graph, where the ordinates are molecular concentrations of $Ca(HCO_3)_2$ and the abscissas cube roots of molecular concentrations of free H_2CO_3, all free carbon dioxide in the solution being calculated as H_2CO_3. A few nearly coinciding points have been omitted. Fifteen experiments were made in glass bottles at pressures of carbon dioxide between 0.06 and 1 atmosphere. Twenty-one experiments were made in the steel bottle at pressures between 2 and 25 atmospheres. These values are not actual measured pressures but are those calculated from the solubility at atmospheric

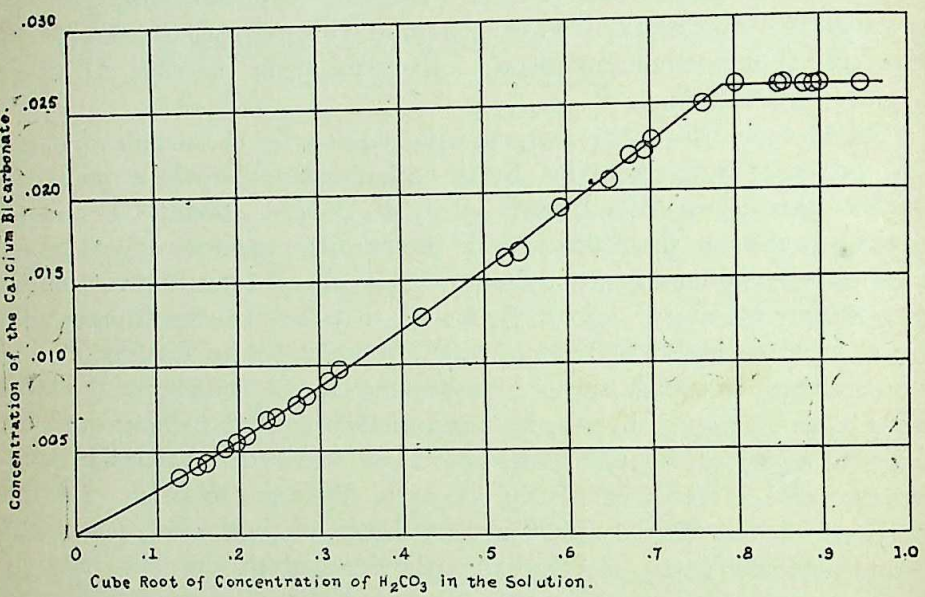
[1] Winkler's method, see Küster, *Z. anorg. Chem.*, 13, 127 (1897).

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pressure[1] by Henry's law, which, however, does not apply closely for carbon dioxide as shown by Wroblewski.[2]

As shown by the graph, a maximum solubility of calcium salt is reached at a certain concentration of carbonic acid. This is 0.485 normal molecular and corresponds to a calculated carbon dioxide pressure of about



15 atmospheres. The obvious interpretation is that the solution becomes saturated with $Ca(HCO_3)_2$ at this point. This saturated solution is 0.026 molecular, equal to 0.42 g. of $Ca(HCO_3)_2$ per 100 cc. Theoretically it should be possible to convert all of the solid $CaCO_3$ present (about 100 g.) into solid bicarbonate by introducing carbon dioxide in sufficient amount at a pressure greater than 15 atmospheres. As long as any solid $CaCO_3$ remained the pressure of carbon dioxide should finally fall to 15 atmospheres. It was found, however, that pressures between 16 and 25 atmospheres remained at the end of 2 or 3 days' rotation of the steel bottle and that the solid residue was still largely, if not wholly, $CaCO_3$. This would seem to show that our interpretation is incorrect. But when we consider that about 2 days are required to dissolve the 2 g. of $CaCO_3$ necessary to saturate the solution at its maximum concentration, we could not expect to accomplish the complete conversion of the CO_2 and $CaCO_3$ into bicarbonate in less than 3 months. We are inclined to think, therefore, that when we can give the reaction sufficient time we shall find the facts in harmony with the hypothesis.[3] This hypothesis is also

[1] Just, *Z. physik. Chem.*, 37, 342 (1901); Geffcken, *Ibid.*, 49, 273 (1904).

[2] *Compt. rend.*, 94, 955, 1355 (1882).

[3] This investigation had to be discontinued in Aug., 1910. We hope to resume it in the near future.

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supported by the experiments of Keiser[1] who found that an unstable precipitate was formed by the action of NH_4HCO_3 on a cold solution of $CaCl_2$. The precipitate had the approximate composition $CaCO_3$ 1.75H_2CO_3 and was evidently impure calcium bicarbonate. It is now easy to explain why the precipitate decomposed so readily: its decomposition pressure was much greater than 1 atmosphere.

The numerical results of 6 typical experiments of the 36 completed are given in the following table:

Approx. pres. CO_2 in atmos.	1000 H_2CO_3.	1000 $Ca(HCO_3)_2$.	100 α.	1000 k.
0.1	3.522	4.116	86.6	23.4
1.1	37.28	9.734	81.0	23.6
9.9	332.9	22.36	72.8	23.5
13.2	444.	24.95	71.3	23.3
16.3	550.	26.00	....	....
25.4	858.	26.03	....	....

The calculated approximate pressures are not to be considered as accurate. The concentrations of H_2CO_3 and $Ca(HCO_3)_2$ were found by analysis as described. In the fourth column, α is the assumed degree of ionization of $Ca(HCO_3)_2$, which is taken to be the same as that of calcium acetate at the same concentration, the values given having been calculated from the figures given by Kohlrausch and Holborn,[2] p. 161. The equilibrium constant, k, was calculated by equation 6.

$$k = \frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}}$$

The mean value of k for the 29 experiments at pressures less than 15 atmospheres, where the solutions were unsaturated with $Ca(HCO_3)_2$, was 0.0234; the maximum was 2.5 per cent. higher; the minimum was 2.5 per cent. lower; the average deviation from the mean was 1.0 per cent. The 7 experiments at pressures greater than 15 atmospheres all gave essentially identical concentrations of $Ca(HCO_3)_2$. This fact is illustrated by the last two results given in the table and is clearly shown by the graph. Naturally, these 7 experiments may not be used to calculate the equilibrium constant. Seyler and Lloyd's experiments on the solubility of $CaCO_3$ in aqueous carbonic acid were made at "room temperature." Their equilibrium constant, F, bears to ours the relation

$$k = 0.02\sqrt[3]{F}.$$

Their average value of $F = 113$ substituted in the above equation gives $k = 0.0242$; our own experiments gave 0.0234.

In equation (6) k_3, the solubility product of $CaCO_3$, is expressed in terms of k, the equilibrium constant determined by this investigation and k_1

[1] This Journal, 30, 1711 (1908).

[2] Leitvermögen, Leipzig, 1898.

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and k_2, the primary and secondary ionization constants of carbonic acid. Rearrangement of (6) gives

$$(7) \qquad Ca \times CO_3 = k_3 = 4k_2k^3/k_1.$$

The constant k_1 was determined by Walker and Carmack[1] by conductivity measurements to be 3.04×10^{-7}. The secondary constant, k_2, is not known with the same degree of accuracy as k_1. Experiments by one of us[2] on the equilibrium between Na_2CO_3, $NaHCO_3$, CO_2 and H_2O give the only available data for the calculation of k_2. From the results with 0.1 N solutions, the original calculation gave the value $k_2 = 6.04 \times 10^{-11}$. The subsequent work of Geffcken[3] on the effect of salts on the solubility of carbon dioxide gave data from which Stieglitz corrected the calculation and found $k_2 = 6.20 \times 10^{-11}$. For some unknown reason, more concentrated sodium carbonate solutions gave considerably higher values: for 0.3 N solutions $k_2 = 7.8 \times 10^{-11}$. Normal solutions gave still higher values. Extrapolation gives $k_2 = 5.4 \times 10^{-11}$ for an infinitly dilute solution and 5.5×10^{-11} for a solution 0.02 N. As the solutions of $Ca(HCO_3)_2$ were from 0.003 to 0.026 N we shall use in the following calculations $k_2 = 5.5 \times 10^{-11}$. Substitution of this value in equation (7) gives $k_3 = 9.3 \times 10^{-9}$. Stieglitz used $k_2 = 7 \times 10^{-11}$ and obtained from Schloessing's experiments $k_3 = 12.6 \times 10^{-9}$. If we use the same value of k_2, our experiments give $k_3 = 11.9 \times 10^{-9}$. We think that the lower value of k_2, and therefore also of k_3, is preferable. Seyler and Lloyd point out that k_2, the secondary constant for carbonic acid, decreases with decreasing concentration of the sodium carbonate solutions used in its determination by McCoy's method. For this reason they did not try to calculate the solubility product of $CaCO_3$. They have undertaken a new determination of k_2 but the results are apparently not yet published.

If $CaCO_3$ were not hydrolytically dissociated, the concentration of Ca (equal also to CO_3) in pure water, free from CO_2, would be $k_3 = 9.6 \times 10^{-5}$ or 9.6 mg. per liter. It is now possible to calculate the concentrations of the components of such a solution, when hydrolytic dissociation is taken into account. In addition to equations (1), (2) and (3) the following relations also exist:

$$(8) \qquad H \times OH = k_w$$

$$(9) \qquad H + 2Ca = OH + HCO_3 + 2CO_3,$$

since the solution is electrically neutral. This reduces to

$$(10) \qquad 2Ca = OH + HCO_3 + 2CO_3$$

by reason of the negligibly small value of H compared with $2Ca$.

[1] *J. Chem. Soc.*, **77**, 5 (1900).
[2] McCoy, *Loc. cit.*
[3] *Loc. cit.*

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Finally,

$$Ca = HCO_3 + CO_3 + H_2CO_3 \quad (11)$$

if there is no excess or deficiency of CO_2. The six equations give

$$\frac{H^4(2H + k_1)^2}{H^2 + k_1H + k_1k_2} = \frac{k_1k_2k_w^2}{k_3}. \quad (12)$$

The solution of (12) gives $H = 1.09 \times 10^{-10}$, from which we then find $Ca = 1.66 \times 10^{-4}$; $CO_3 = 0.56 \times 10^{-4}$; $H_2CO_3 = 1.10 \times 10^{-4}$; $OH = 1.10 \times 10^{-4}$; $H_2CO_3 = 4.0 \times 10^{-8}$. An inspection of the figures shows that a solution formed from pure water and $CaCO_3$ would contain only 34 per cent. as much free CO_3 as the Ca present would represent. The remaining 66 per cent. of the CO_3 would have united with water to give HCO_3 and an equal concentration of OH. To form such a solution 16.6 mg. of $CaCO_3$ per liter of water would be required if practically complete ionization be assumed. We have calculated from the measurements of Kohlrausch[1] of the conductivity of pure water saturated with $CaCO_3$ that 12 mg. of the substance are dissolved by 1 l. of water. In so doing we have considered the hydrolysis to be 66 per cent. The agreement is only fair; the cause of the difference is not apparent.

Strontium and barium carbonates have been studied in the same way as calcium carbonate. In the case of strontium carbonate, nine experiments have been made at pressures between 0.05 and 1.1 atmospheres. The equilibrium constant $k = 1.29 \times 10^{-2}$, with an average deviation from the mean of 1.2 per cent. This value leads by equation (7) to the solubility product $Sr \times CO_3 = k_3 = 1.567 \times 10^{-9}$. With barium carbonate, eleven experiments were made at pressures between 0.2 and 30 atmospheres. The graph for $BaCO_3$ is very similar to that for $CaCO_3$; a maximum solubility, $Ba(HCO_3)_2 = 0.028$, is reached at a concentration of $H_2CO_3 = 0.727$, corresponding to a calculated CO_2 pressure of about 22 atmospheres. The solubility of $Ba(HCO_3)_2$ is 7.3 g. per liter or 0.73 g. in 100 cc. of water. For $BaCO_3$ the equilibrium constant was found to be $k = 2.24 \times 10^{-2}$; average deviation from mean = 0.8 per cent. The solubility product $Ba \times CO_3 = k_3 = 8.1 \times 10^{-9}$.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

EQUILIBRIUM BETWEEN SODIUM CARBONATE, SODIUM BICARBONATE AND WATER.

[SECOND PAPER.]

BY HERBERT N. MCCOY AND CHARLES D. TEST.

Received January 25, 1911.

Several years ago one of us made a study of the system carbonates of sodium, carbon dioxide and water,[2] for solutions of decinormal to normal

[1] *Z. physik. Chem.*, 44, 236 (1903).

[2] McCoy, *Amer. Chem. J.*, 29, 437 (1903).

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concentration. We have now extended this work to include solutions in equilibrium with solid phases. All experiments were carried out at 25° ± 0.02. Forty grams of pure sodium bicarbonate and about 200 cc. of water were rotated in a 25° thermostat until equilbrium was reached (usually 24 to 48 hours). Small portions of the clear solution were then analyzed by Winkler's method for carbonate content and by titration in the presence of methyl orange for sodium. About 15 g. of normal sodium carbonate decahydrate were then added to the residual mixture of saturated solution containing solid bicarbonate; the whole again rotated until a new state of equilibrium were reached and again analyzed. The results obtained by a continuation of this method are shown in the accompanying graph, where the ordinates are gram of sodium per cc. of solution and the abscissas are percentages of total sodium in form of bicarbonate in the solution. The following table gives the numerical data for points A, B, C, and D.

	Percentage of sodium as bicarbonate.	Grams of sodium per liter.	Grams of bicarbonate per liter.	Grams of carbonate per liter.
A.....	100.00	27.02	98.7	0.0
B.....	12.89	108.0	50.8	216.6
C.....	5.92	127.6	27.6	276.3
D.....	0.00	119.9	0.0	276.4

The point A represents the solubility of pure sodium bicarbonate in water. AB is the solubility curve for solutions containing increasing proportions of normal carbonate in equilibrium with sodium bicarbonate as the solid phase. At B 12.9 per cent. of the sodium in solution is in the form of bicarbonate and 87.1 in form of carbonate. At this point a new solid phase appears. It consists of long needles. There are therefore four-phases present at the point B: vapor, solution, solid bicarbonate and the needles. The addition of more and more solid sodium carbonate to this four-phase system at B did not change the composition of the solution until all of the solid bicarbonate had disappeared. The solution then contained less than 12.9 per cent. of the sodium as bicarbonate while but one solid phase remained. This consisted of the pure needle form, which after being drained and dried in a centrifuge had the composition $NaCO_3.NaHCO_3.2H_2O$, as shown by the following analysis:

	Calculated.	Found.
Na_2CO_3.....	46.90	46.59
$NaHCO_3$.....	37.17	35.72
$2H_2O$.....	15.93	17.69

The considerable differences between the percentages found and calculated is due to the fact that it was impossible, owing to the nature of the salt, to free the crystals completely from the mother liquor which contained but 10 per cent. of the sodium as bicarbonate.

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Between B and C only one solid phase, the double salt, $Na_2CO_3.NaHCO_3.2H_2O$, is present. At C $Na_2CO_3.10H_2O$ is also present, giving again a four-phase system, of which the solution has a fixed composition, with 5.9 per cent. of the sodium as bicarbonate. Solutions containing smaller proportions of the sodium as bicarbonate give the line CD, the solid phase being $Na_2CO_3.10H_2O$.

The mineral trona or urao, which occurs as a natural deposit from the waters of some alkali lakes, is a more or less pure form of the sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$. In earlier times this natural soda was thought to be $Na_2CO_3.2NaHCO_3$ with varying proportions of water. The correct formula was first given by Laurent:[1] Chatard[2] has made an exhaustive study of natural soda, especially as it occurs at Owen's Lake, Calif. His papers contain extensive references to the literature of the subject.[3]

A number of methods for the artificial preparation of the sesquicarbonate are found in the literature.[4]

All are more or less indefinit or involve the addition of a foreign substance, as common salt. Since the sesquicarbonate, in which $33^1/_3$ per cent. of the sodium is in the form of bicarbonate, is stable in contact with aqueous solutions only when these contain between 12.9 and 5.9 per cent. of the total sodium as bicarbonate it is plain why it is decomposed by water and can not be recrystallized in the ordinary way. This fact explains the difficulties that have been encountered in the artificial preparation of the substance.

Our experiments lead to the following method of preparation: 42 g. of bicarbonate and 700 g. of carbonate decahydrate are dissolved in enough water to make one liter of solution. This solution contains about 10 per cent. of its sodium as bicarbonate. Its composition corresponds to a point between B and C on the graph. If now sodium carbonate, bicarbonate and water in the proportions indicated by the formula $Na_2CO_3.NaHCO_3.2H_2O$ be added to the above solution, and the whole shaken at 25°, all of the materials last added will unite to form needles of the sesquicarbonate. The mother liquor may be used repeatedly with new portions of material.

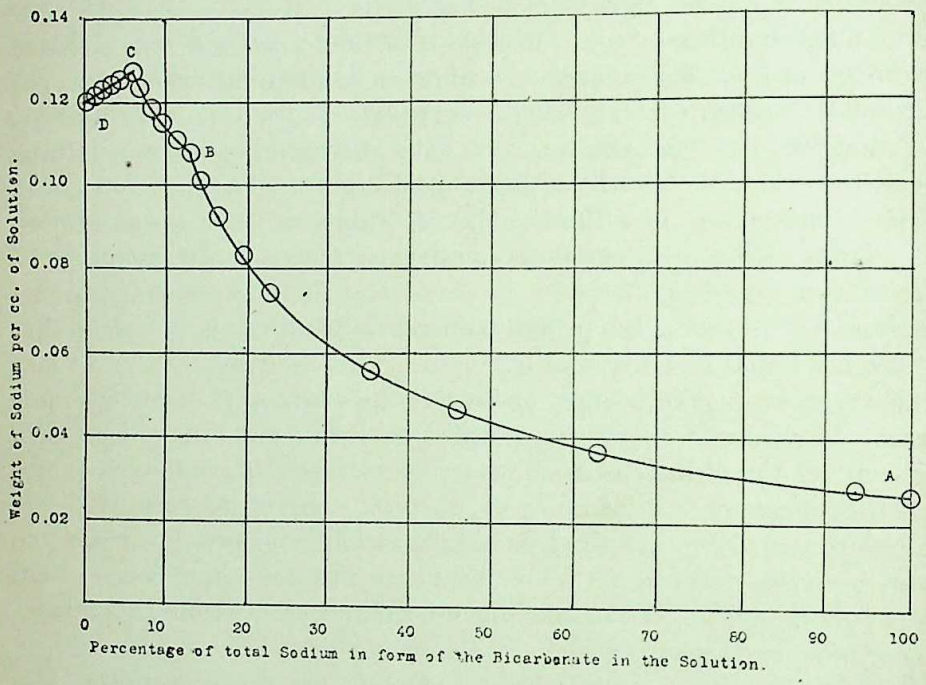
The interpretation of the results from the standpoint of the phase rule is very simple. The system has three components. Since the temperature is fixed (25°) the maximum number of phases is four. This condition is fulfilled at the points B and C. At B, there are in addition

[1] *Ann. chim. phys.*, [3] 36, 348 (1852).
[2] U. S. Geol. Survey., *Bull.* 60, 27 (1887); *Am. J. Sci.*, 38, 59.
[3] See also Lunge, *Z. angew. Chem.*, 1893, 3.
[4] Mondesir, *Compt. rend.*, 104, 1505 (1887); Watts and Richards, D. R. P., 43, 583; Chatard, *Loc. cit.*; Winkler, *Répert.*, 48, 215; *Z. angew. Chem.*, 1893, 445, 599.

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to the liquid and vapor phases, two solid phases: bicarbonate and sesquicarbonate. At C, the two solid phases are sesquicarbonate and normal carbonate decahydrate. Each of the three curves represents a three-phase system, each having a vapor, a liquid and a solid phase. Along AB the solid is the bicarbonate; along BC it is the sesquicarbonate; along



CD the decahydrate of the normal carbonate. We have made preliminary determinations of the concentration of carbon dioxide in the vapor in equilibrium with solutions of various bicarbonate content. The concentration is high at A and decreases rapidly toward B. When air is drawn through a saturated solution of bicarbonate, in contact with an excess of the solid, the solution loses carbon dioxide: at first rapidly, later very slowly. In six weeks, at 25°, the composition of the solution changed along the curve AB until the solution contained only 18 per cent. of its sodium as bicarbonate. The rate of change was now very slow, but equilibrium had not been reached.

[Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 66.]

THE HEAT CONTENT OF THE VARIOUS FORMS OF SULFUR.

By Gilbert N. Lewis and Merle Randall.

Received February 22, 1911.

In a systematic calculation of the free energy of the sulfur compounds, we have found it necessary to know, with some degree of precision, the

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energy changes involved in the conversion of the various forms of sulfur into one another, as well as the specific heat of the several forms. The specific heat of the two crystallin forms of sulfur and the heat of transformation of the one into the other have been determined with sufficient accuracy by previous investigators, but the data on the heat of fusion of the two crystallin modifications are in need of revision, and no reliable determinations of the specific heat of liquid sulfur are to be found in the literature. The present investigation, while undertaken primarily to provide necessary material for the calculation of free energy, possesses a certain interest of its own, on account of the very abnormal conditions which have been shown to exist in liquid sulfur.

It is well known that liquid sulfur is composed of two substances, the relative amounts of which, in equilibrium with each other at a given temperature, may be obtained by suddenly chilling the liquid under suitable conditions. One of the substances known as S_λ yields thus a product which is soluble in carbon bisulfide, and the other, S_μ, one which is insoluble, or rather, one which dissolves with no measurable speed. The relative amounts of these two, in equilibrium with each other at different temperatures, have recently been determined by Smith and his collaborators,[1] and their results have been plotted in Fig. 1. The percentage of S_μ, or insoluble sulfur, which is plotted from left to right, increases from about 4 per cent. at 120° to about 34 per cent. at 445°, the greater part of the change taking place within a comparatively narrow temperature range in the neighborhood of 160°.

From the form of this curve, it is evident that in case the change from S_λ to S_μ is associated with a considerable energy change, the specific heat of liquid sulfur, when it is heated in such a way as to maintain equilibrium between the two forms, must vary with the temperature in a very unusual manner. Wigand[2] has attempted to calculate the heat associated with the change from S_λ to S_μ by introducing the data which we have reproduced in Fig. 1 in the van't Hoff equation,[3]

[1] Smith and Holmes, *Z. physik. Chem.*, 54, 257 (1905); Carson, THIS JOURNAL, 29, 499 (1909). A comprehensive bibliography of the earlier work on this subject is given by Kruyt, *Z. physik. Chem.*, 64, 513 (1908).

[2] Wigand, *Z. physik. Chem.*, 63, 273 (1908).

[3] This procedure was first suggested by Schaum, *Ann.*, 308, 23 (1899). Smith and Holmes, *Z. physik. Chem.*, 54, 267 (1905), attempted to apply this method of calculating the heat of reaction but concluded that it was incorrect, giving as their reason that the equation of van't Hoff, being derived from the laws of dilute solutions, could not be expected to hold in a system containing only the two reacting substances and no other solvent. This is not identical with the explanation which we offer here, for the equation of van't Hoff would be rigorously applicable to this case, no matter what the relative amounts of the two varieties of sulfur might be, if these formed perfect solutions with each other. For a discussion of the definition of a perfect solution see Lewis, THIS JOURNAL, 30, 668 (1908).

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$$\frac{d \ln K}{dT} = \frac{U}{RT^2}.$$

In this equation K is the ratio of S_μ to S_λ, in equilibrium, and U is the heat absorbed when eight gram-atoms of sulfur pass from the soluble to the insoluble form (the formula of both forms of liquid sulfur is assumed to be S_8). From the rate of change in the relative amounts of S_μ and S_λ, at 130°, Wigand obtains at this temperature 21.1 cal. per gram for the heat of the reaction in question. That this value is not

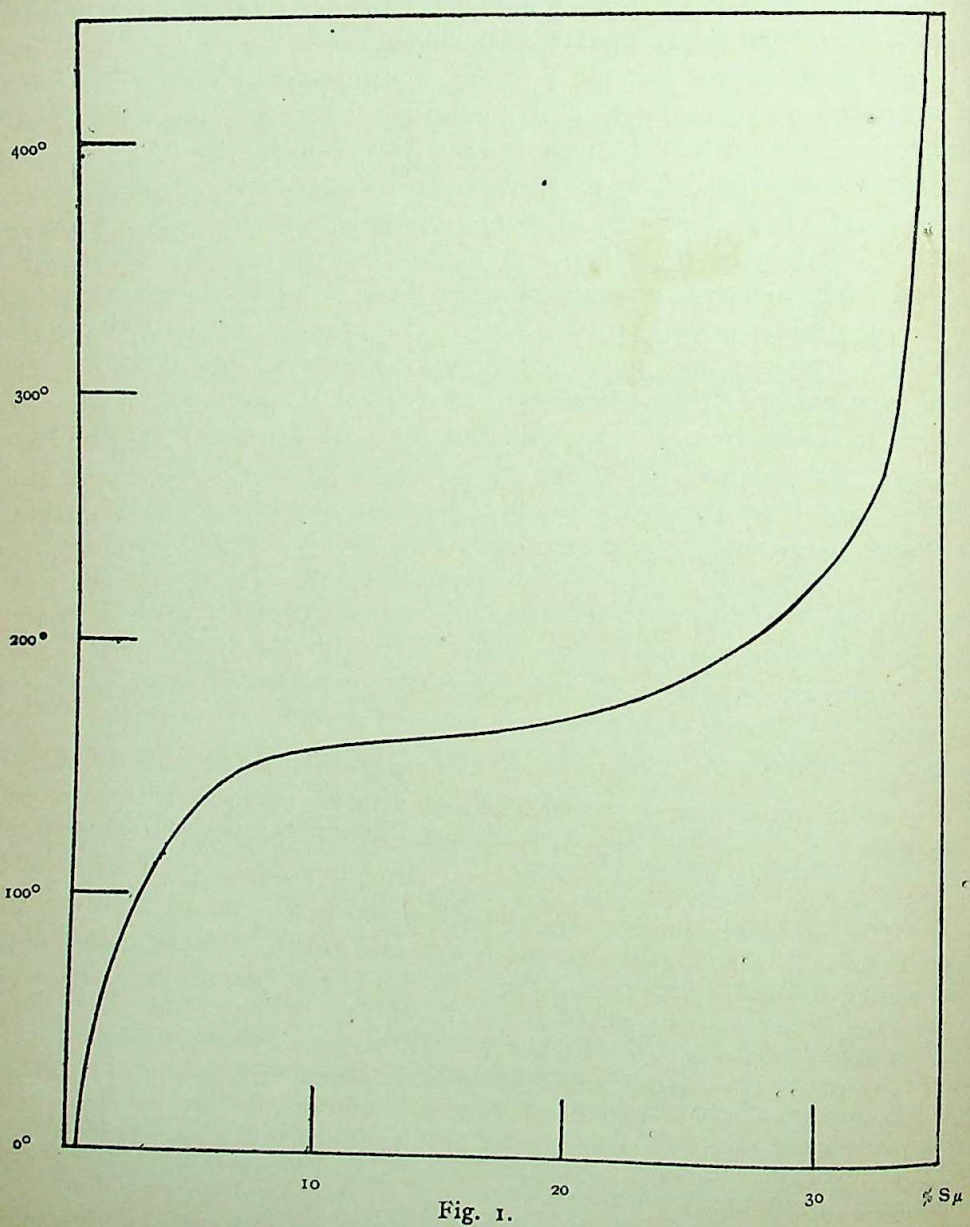


Fig. 1.

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far from the one which will be obtained below from calorimetric measurements is the merest accident, for if Wigand had used other temperatures, his method would have given far different results, ranging from 2 or 3 cal. to a maximum value of 146 cal. per gram at 159.5°. Of course, the true heat of the reaction can hardly change much in so small a temperature range, and the calculation of Wigand must, therefore, be erroneous. This is due to the fact that the above equation of van't Hoff is only true in such a case as this, when the substances entering into the reaction obey the laws of the perfect solution. That a mixture of S_μ and S_λ is not a perfect solution may be deduced from the fact that these two liquids are not under all conditions completely miscible. We may, therefore, regard the heat of this reaction as completely unknown.

The Total Heat of Sulfur between 23° and the Temperatures 100°, 140°, 184° and 390°.

In order to determin the specific heat of liquid sulfur and the effect upon it of the transformation of one form of liquid sulfur into the other, molten sulfur was dropped from a constant-temperature bath into a calorimeter at about 23°. The sulfur was of the best quality obtainable from Kahlbaum and was prepared for use in the following manner: A suitable quantity of the crystals was melted in a glass tube and a current of dry ammonia was bubbled through it. It was then allowed to cool, and solidify. The glass tube above the sulfur was then drawn out and attached to a high-vacuum pump. After exhaustion dry ammonia gas was allowed to enter from a bulb containing a solution of ammonium nitrate in liquid ammonia (Divers' solution). The tube containing the sulfur was then sealed off and weighed. The presence of ammonia was shown by Smith, Holmes and Hall,[1] and by Carson[2] to catalyze not only the conversion of one form of liquid sulfur into the other, but also the formation of crystallin sulfur from the insolubl sulfur at room temperatures.

The tube containing sulfur was suspended from a fine wire and introduced[3] into the heating apparatus shown in Fig. 2, and constructed as follows:[4] The concentric iron tubes AA and CC and the plate BB were welded together in the oxy-acetylene flame, forming an annular vessel to contain a boiling liquid. Into the upper end of CC was likewise welded a very small tube, D, through which runs the wire E supporting the sulfur

[1] Smith, Holmes and Hall, *Ber.*, 35, 2992 (1902); THIS JOURNAL, 27, 797 (1905); *Z. physik. Chem.*, 52, 602 (1905).

[2] Carson, *loc. cit.*

[3] In order to prevent the bursting of the tube, owing to the expansion of the sulfur, it was melted cautiously with a free flame before its introduction into the bath.

[4] An apparatus which in several features is not unlike the one which we have employed has been described by White (*Physik. Rev.*, 31, 670 (1910)) while our investigation was under way.

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tube I. The tubes H and J served as condensers and were surrounded by coils of metal tubing carrying running water. A portion of this tubing also passed for a certain distance inside the tubes H and J, making

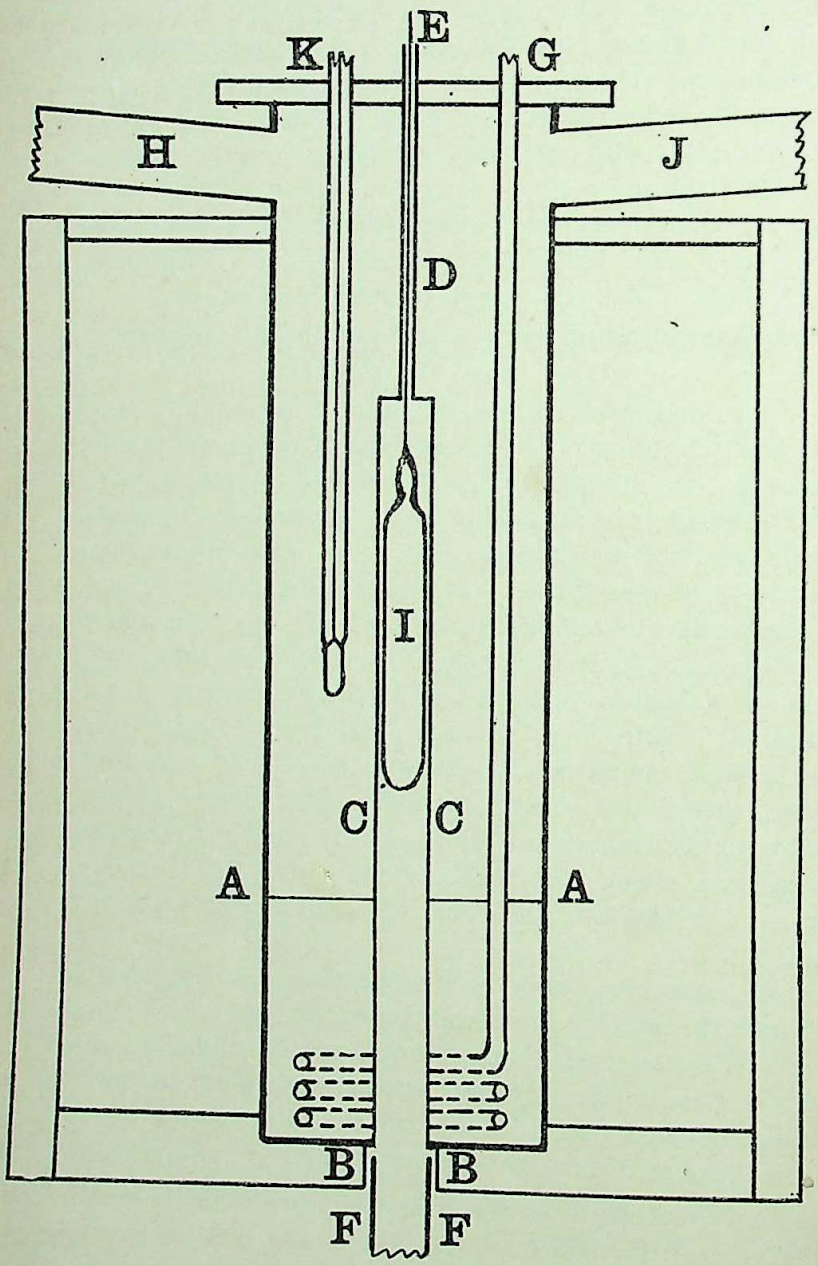


Fig. 2.

the condensation more efficient. The tube AA was wrapped with mica, around which nickel-steel wire was wound, the number of turns being greater at the lower end of the tube. A current of electricity through

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this wire helped to maintain the desired temperature, while the main heating was furnished by an electrical heater, G, of the "Simplex"[1] form. The bath was well lagged with asbestos and furnished with an asbestos cover supporting the thermometer K. The temperature was constant throughout the tube CC, except for a few centimeters at the bottom, as was shown by a thermometer introduced from below. In order to avoid any draft through the small tube D its upper end was joined to a rubber tube which was closed by a pinchcock except at the moment when the wire E was to be released.

This whole apparatus was placed upon a wooden support 45 cm. above the top of the calorimeter, and the tube CC was continued by a glass tube, FF, of the same size which extended to within 2 cm. of the top of the calorimeter. The latter consisted of a Dewar tube of about 800 cc. capacity in which were placed a Beckmann thermometer, a vigorous rotary stirrer, operated by a motor, and a nearly cylindrical metal cage composed of a number of vertical wires connected at the bottom through a brass plate, and fastened at the top to the calorimeter cover of vulcanite. A circular hole in this cover was situated just above the metal cage and below the tube FF. This hole was itself covered by a disk of vulcanite except at the moment when the sulfur tube was lowered into the cage of the calorimeter. The calorimeter was conveniently mounted on a sort of sliding track so that it could be removed from under the heater between experiments.

The experiments were conducted in the customary way, the calorimeter containing a weighed quantity of water was placed under the heater, the stirrer started, and after a suitable time the temperature was read every minute for 6 to 10 minutes. The substance contained in the heating bath was then dropped.[2] The temperature readings were then continued at intervals of a minute until a constant rate of cooling was reached.

The first experiments were made with a bath of boiling xylene at temperatures ranging from 139.6° to 140.2°, depending upon the atmospheric pressure.

In order to calibrate the calorimeter and thermometer, several tubes containing water were first dropped from the xylene bath into the calorimeter. Ten experiments were made with three different tubes of water. In two cases the tube containing water burst on striking the calorimeter, a third experiment was lost through faulty lowering of the tube. Of the remaining seven, two gave results which were obviously inconsistent with the others and were doubtless due to our lack of experience with the apparatus. The remaining five gave results in which the average

[1] Manufactured by the Simplex Elec. Heating Co., Cambridge, Mass.

[2] The substance was not actually dropped but was rapidly lowered into the calorimeter. The time of fall was from two- to three-fifths of a second.

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deviation from the mean was 0.3 per cent. This figure probably gives a fair measure of the reproducibility of determinations with this calorimeter.

In order to compare these results with one another and to determin the constant of the calorimeter, it was necessary to know the specific heat of water and of the glass used. The specific heat of water has been taken from the formula of Callender[1] which is based chiefly on the experiments of Barnes and of Regnault. This gives for the total heat of one gram of water from 23° to 140°, 117.46 cal.[2] The specific heat of the particular specimen of glass tubing employed, which was a common soft sodium glass made in Germany, we determined directly in three experiments which gave as a mean for the specific heat of this glass between 23° and 140°, 0.2057.[3]

From these data we find that when the calorimeter contains 690 grams of water, 736.1 cal. produce a rise of one degree in the Beckmann thermometer, showing that the heat capacity of the calorimeter is about 47 cal. per degree.

Experiments were next made with a number of tubes of the same glass containing sulfur. The weight of the sulfur ranged from 25 to 35 grams and that of the glass from 15 to 20 grams. The sulfur was kept in the bath from one and a half to three hours. The results of five experiments with three different tubes are given in Table I. The third column shows the total heat given to the calorimeter per gram of sulfur, after allowance is made for the heat of the glass.

TABLE I.—140–23°.

No. of expt.	No. of tube.	Total heat: cal. per gram sulfur.
1	1	37.76
2	2	38.42
3	2	37.93
4	2	38.08
5	3	38.00
	Average,	38.04

A fourth tube gave results quite inconsistent with the others, namely, 34.01, 33.31, 32.23. This discrepancy is far too great to be due to any calorimetric error. Since some of these tubes were prepared before the best means of treating the sulfur with ammonia had been found it seemed likely that an insufficiency of ammonia in the fourth tube might be respon-

[1] Callender, *Trans. Roy. Soc., A.* 199, 55 (1902).

[2] We shall use throughout the common calorie, that is, the heat required to raise one gram of water from 15° to 16°.

[3] This is very near to the value 0.2040 obtained by White, *Am. J. Sci.*, [4] 28, 334 (1909), over the same range for a similar glass. At other temperatures, therefore, we have used the temperature coefficient obtained by White.

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sible for the results obtained. In order to test this hypothesis two other tubes were prepared which were previously treated with sulfur dioxide instead of ammonia, since Carson[1] has shown that sulfur dioxide has an effect opposit to that of ammonia, retarding the establishment of equilibrium conditions. These two tubes gave for the total heat of sulfur, 32.74 and 33.04, respectively. Since both of these tubes broke in the calorimeter the experiments are probably not entirely conclusive but appear to show the correctness of our theory of the discrepancy in the case of tube four. The sulfur in the first three tubes appeared after each experiment to be in the form of rhombic sulfur and this view was corroborated by some experiments which will be described below. One of these tubes after being dropped into the calorimeter was broken and the sulfur was found to be almost completely soluble in carbon disulfide. We will therefore take 38.04 cal. per gram as the difference in internal energy between liquid sulfur at 140°, and rhombic sulfur at 23°.

The next experiments were made with a bath of aniline, boiling at 184°. The first five experiments gave for the total heat of sulfur per gram between 184° and 23°, the values 47.59, 50.74, 48.64, 50.99 and 48.55. In every case but the second the glass-containing tube broke, and the sulfur flowed to some extent into the calorimeter cage before solidifying. Here also the differences are too great to be regarded as calorimetric errors.

Before studying this matter further several experiments were made in a bath of boiling water at 100°. Sulfur when once liquefied is readily supercooled and the tubes could be kept at 100° for any desired time without crystallization. The first two experiments gave the total heat between 100° and 23° as 29.00 and 29.04 cal. In both cases a distinct change was noticed in the cooling curve, due apparently to a process evolving heat which began when the contents of the calorimeter had nearly reached uniform temperature, and lasted for five or ten minutes, after which a constant rate of cooling was again obtained. This phenomenon was so marked in the third experiment that a constant rate of cooling had been reached before the secondary reaction began, so that the total heat evolved in the calorimeter could be divided into two distinct portions. The sum of the two per gram of sulfur was 28.34 cal. while the first portion was only 25.85 cal. The same tube was again heated and dropped, and as soon as it reached its first constant cooling rate it was removed from the calorimeter and found to contain a form of sulfur entirely different in appearance from the yellow, opaque substance obtained previously. It was amber-colored, translucent and showed the long prismatic crystals characteristic of monoclinic sulfur. Presently at one end of the tube the sulfur began to change to the yellow, opaque form, and this change

[1] Carson, THIS JOURNAL, 29, 499 (1909).

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progressed rapidly through the tube until in a few minutes the conversion was complete. The total heat per gram given to the calorimeter in this experiment was 25.50 cal., and of course did not include, as in the other cases, the heat of transition from the amber-colored sulfur to the yellow sulfur. Further experiments showed that the amber-like sulfur changed to the other form more rapidly at higher temperatures, but when a tube in which the conversion was partially completed was plunged into boiling water the transformation ceased and did not recommence until the tube was partially cooled. This experiment showed conclusively that the two forms of sulfur under consideration were the rhombic and monoclinic, of which the transition point is 95°.

In four experiments the values for the total heat per gram from liquid sulfur at 100° to rhombic sulfur at 23° were 29.00. 29.04, 28.34 and 28.24 with an average of 28.65. Two experiments gave as the total heat per gram between liquid sulfur at 100° and monoclinic sulfur at 23°, the values 25.97 and 25.50 with an average of 25.74.

The difference between these two means, namely 2.91 cal., should be the heat of transition of monoclinic to rhombic sulfur at 23°, although, of course, this is not an accurate method for the determination of this quantity, since the heat of transition appears as a small difference between the two quantities experimentally determined. This heat of transition has been determined directly and therefore more accurately by Brönsted[1] at 0° and by Tammann[2] at 95° and their results are in close agreement. From Brönsted's value and the known specific heats[3] of rhombic and monoclinic sulfur the heat of transition at 23° is 2.54 cal. Assuming this value to be correct we may add it to the total heat obtained in the two cases where monoclinic sulfur was the final product, and thus obtain two additional values for the total heat between liquid sulfur at 100° and rhombic sulfur at 23°, namely 28.51 and 28.04 cal. These values, averaged with the four given above, give a final mean of 28.53.

From the specific heat of rhombic sulfur the total heat of this substance between 23° and 100° is 13.66 cal. By subtracting this value from the one we have just obtained above we find 14.87 cal. as the heat of fusion of rhombic sulfur at 100°. The heat of transition between rhombic and monoclinic sulfur at this temperature from the data previously mentioned is 3.36 cal. and therefore 11.51 cal. is the heat of fusion of monoclinic sulfur at 100°.

It must be borne in mind that these are the heats of fusion when the solid is converted into liquid sulfur in which S_λ and S_μ are in equilibrium.

[1] Brönsted, *Z. physik. Chem.*, 55, 371 (1906).

[2] Tammann, *Kristallisieren und Schmelzen*, 275 (1903).

[3] The specific heat of rhombic sulfur is taken as $0.168 + 0.00015t$, and of monoclinic sulfur as $0.174 + 0.00022t$ where t is temperature centigrade. The complete data from which these values are taken will be discussed in another paper.

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These values are therefore higher than those which would be obtained by merely fusing the crystallin substances to form pure S_λ. The difference is the heat of conversion of about 0.03 gram of S_μ into S_λ. From the calculations which we give below this proves to be 0.4 cal. The heats of fusion of rhombic and monoclinic sulfur to form pure S_λ at 100° are therefore 14.5 and 11.1 respectively. For the latter quantity Wigand[1] gives a résumé of the results of previous investigators. His own value is 10.4 cal. at 119° which is equivalent to 9.8 cal. at 100°. Although Wigand used a direct method, his four values show an average deviation from the mean of 5.7 per cent., and his highest value agrees with ours. It is hardly likely that our value can be in error by more than 2, or perhaps 3 per cent.

Returning now to the experiments at 184°, two more experiments were made in which the sulfur was examined as soon as possible after the calorimeter came to a constant rate of cooling. In both cases the glass containing tube broke in the calorimeter. In the first experiment the greater part of the sulfur appeared in a form which we have not seen described hitherto. It was glassy, brittle, almost colorless, and appeared to be noncrystallin. Inside of the glassy shell was a considerable amount of rhombic sulfur. This experiment gave for the total heat per gram 47.86 cal. The next experiment was similar except that the percentage of glassy sulfur was relatively small, the greater part being rhombic. The total heat per gram for this experiment was 49.93 cal. These results entirely corroborated a view to which we had been led by the preceding experiments, namely that the two experiments in which the result was high, 50.74 and 50.99, were the only ones in which pure rhombic sulfur was the end product. In one of these the glass containing tube remained intact and there can be no question that the product was pure rhombic sulfur. In the other cases the values were smaller, apparently by an amount dependent upon the percentage of glassy sulfur which was formed. We shall therefore take the average of 50.74 and 50.99, namely, 50.86, as the total heat per gram between liquid sulfur at 184° and rhombic sulfur at 23°.

It seemed advisable to make a few experiments with a bath at a much higher temperature, and for this bath we chose a substance known as retene, the boiling point of which was 391°, according to a standardized mercury thermometer, and 388°, according to a calibrated copper-constantan thermocouple. The average was assumed to be correct and as the temperature varied slightly in the different experiments the results were all calculated to 390°. We hoped to avoid the breaking of the containing tubes by using a special borosilicate glass[2] of very small coefficient of

[1] Wigand, *Z. physik. Chem.*, 63, 273 (1908).

[2] Known as HH glass, and manufactured by the Corning Glass Works, Corning, N. Y.

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expansion, but partly perhaps because the glass was old this precaution did not suffice. Since a smaller amount of sulfur was dropped in these experiments, it was necessary to attach to the tube a gold weight of 43 grams, to make the tubes sink rapidly into the calorimeter.

In order to allow for the specific heat of this glass and the gold, as well as for any constant error due to loss of heat in dropping the tube, two blank experiments were made with glass tube and gold weight alone. The gold weight of 43 grams and glass tube weighing 13.81 grams gave 1694 cal. to the calorimeter at 23°. The experiments with sulfur were not altogether satisfactory, owing to the breaking of the glass. The consequent sudden heating of the calorimeter caused an appreciable quantity of steam to be evolved. In several experiments a yellow, rubber-like form of sulfur was obtained, concerning the energy of which we have no information. The first experiment gave only glassy and rhombic sulfur about as in the last two experiments at 184°. The total heat per gram of sulfur was 100.0 cal. The second gave a similar sulfur with a small amount of the rubber-like form. It also gave the value 100.0 cal. The next two experiments gave larger amounts of rubbery sulfur and the values were 99.9 and 95.3 cal. Only the first two experiments deserve much consideration. That they agree so closely is pure accident, for in both cases steam was evolved which we roughly estimate as equivalent to 3 cal. Moreover, the sulfur formed was of the sort which we have previously found to differ in energy from rhombic sulfur by about 2 cal. We shall therefore take 105 cal. per gram as the total heat between liquid sulfur at 390° and rhombic sulfur at 23°.

The values for 390° and 184° will need revision. We believe that with no other change in our procedure except the substitution of quartz for glass tubes extremely satisfactory results could be obtained.

The Specific Heat of Liquid S_λ and the Heat of Transformation of S_λ to S_μ.

We have found for the total heat per gram between liquid sulfur at four different temperatures and rhombic sulfur at 23° the values given in column 2 of the following table. The first column gives the temperatures of the liquid sulfur. The third column gives the changes in total heats between the successive temperature intervals. The fourth column gives this change divided by the temperature interval; in other words, the mean specific heat of the liquid sulfur in each interval. The fifth column shows the percentage of S_μ in the liquid at each temperature, as taken from the plot reproduced in Fig. 1. The sixth column shows the change in this percentage in the successive intervals, and the last column these changes divided by the temperature intervals, or in other words the average change per degree in the percentage of S_μ.

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TABLE II.

t.	Total heat.		Mean sp. heat.	Per cent. S_μ.		Change in per cent. S per degree.
100	28.53			3.1		
		9.51	0.238		2.4	0.060
140	38.04			5.5		
		12.82	0.292		18.2	0.414
184	50.86			23.7		
		54.14	0.263		10.2	0.050
390	105.0			33.9		

The effect of the heat of transformation from S_λ to S_μ on the specific heat is very evident, the specific heat being larger in that interval in which the transformation is taking place most rapidly. In order to form an estimate of the heat of this transformation, we will make the assumption that this heat is nearly independent of the temperature, at least throughout the region of most rapid change, and that the specific heat of S_λ is a linear function of the temperature. We will write then for the specific heat of liquid sulfur at any temperature the equation

$$c = a + bt + q\, dx/dt,$$

where t is the centigrade temperature, a is the specific heat of liquid S_λ at the centigrade zero, b is the change of this quantity with the temperature, q is the heat absorbed when one gram of S_λ is completely converted to S_μ, and x is the fraction of the sulfur which exists as S_μ at the temperature in question. We have evidently in the above table sufficient data for the calculation of the constants of this equation, and we find that $a = 0.21$, $b = 0.00016$ and $q = 13$. In other words we find for the specific heat of liquid S_λ,

$$c = 0.21 + 0.00016\, t,$$

and 13 cal. for the heat of transformation per gram from S_λ to S_μ. This estimate of the heat of transformation is not accurate and may easily be in error by 10 or 15 per cent.

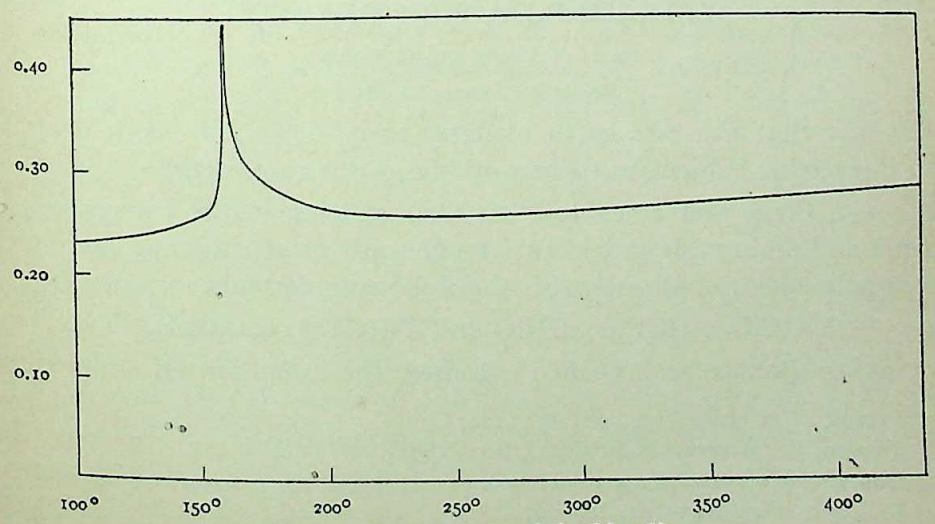


Fig. 3.—Specific heat of liquid sulfur.

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Knowing the value of ζ and the fraction of S_μ at different temperatures we may obtain a rough idea of the change of the specific heat with the temperature, from the above equation. We thus obtain the results plotted in Fig. 3, in which the abscissas represent centigrade temperature, and the ordinates actual specific heats. It will be seen that the specific heat changes very remarkably with the temperature, with a maximum value of 0.44 at about 160°.

It should be noted that all of these results refer to the specific heat of liquid sulfur in the presence of a suitable catalyzer. It is not therefore possible to compare them directly with the values obtained by other observers using sulfur of unknown character. We may refer to the value 0.234 between 119° and 147° obtained by Person,[1] the value 0.232 between 116° and 136° obtained by Classen[2] and several determinations by Dussy.[3]

Summary.

The total heat change is determined between rhombic sulfur at 23° and liquid sulfur (in a state of equilibrium) at the temperatures 100°, 140°, 184° and 390°. From the results obtained the following data are calculated in small calories per gram of sulfur. The heat of fusion at 100°, to form liquid sulfur in a state of equilibrium: from rhombic sulfur 14.9, from monoclinic sulfur 11.5. For the heat of fusion to form pure liquid S_λ: from rhombic sulfur 14.5, from monoclinic sulfur 11.1. For the heat of transformation in the liquid state from S_λ to S_μ, about 13. For the specific heat of pure liquid S_λ about $0.21 + 0.00016\ t$.

A diagram is given showing the approximate values of the specific heat of liquid sulfur, in the equilibrium state, over a range of temperature from 100° to 450°.

YTTRIUM POTASSIUM OXALATE.

By L. A. Pratt and C. James.

Received February 20, 1911.

The fact that the rare earth oxalates carry down the alkali oxalates is an interesting subject to those working on the rare earths.

In 1873, Cleve and Hoeglund,[4] in their articles on the compounds of yttrium and erbium, described two double salts of yttrium and potassium with oxalic acid, and assigned the following formulas (recalculated):

$$Yt_2(C_2O_4)_3.4K_2C_2O_4.12H_2O \text{ and } Yt_2(C_2O_4)_3.K_2C_2O_4.H_2O.$$

In 1906, Baxter and Griffen[5] studied the occlusion of ammonium

[1] Person, *Ann. chim. phys.*, 21, 295 (1847).
[2] Classen, *Z. Instrumentenkunde*, 11, 301 (1891).
[3] Dussy, *Compt. rend.*, 123, 305 (1896).
[4] *Bull. soc. chim.*, 193–201, 289–297.
[5] This Journal, 28, 1684.

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oxalate by the oxalates of the rare earths, and in 1908, Baxter and Daudt[1] extended the work to sodium and potassium oxalates.

In 1907, von Welsbach[2] described a new method for the separation of the yttria earths based on the crystallization of the rare earth ammonium oxalates. He also worked with the sodium double salt and the potassium double salt. The former he found too insoluble and the latter too soluble for obtaining results by fractional crystallization.

Since no systematic study has ever been carried out on this subject, it has seemed to the authors that a careful investigation of the solubility of yttrium oxalate in potassium oxalate solutions and an examination of the accompanying solid phases would be of value.

The purification of the yttrium used for this research was accomplished by the crystallization of the bromates and the fusion of the nitrates, according to a paper by the authors.[3] The pure yttrium thus obtained was converted into the oxalate. A saturated solution of potassium oxalate was prepared from pure potassium oxalate.

Varying amounts of potassium oxalate and yttrium oxalate were added to sufficient water to make about 75 cc., placed in bottles of 100 cc. capacity and rotated in a thermostat at 25° for eight weeks, when equilibrium was proved to have been reached. The bottles were then allowed to stand in the thermostat until the solutions cleared. The settling of the solid phases required only a few hours.

Portions of the supernatant liquids were withdrawn and the yttrium and total C_2O_3 determined. The C_2O_3 was estimated by titration with standard potassium permanganate solution. The determination of the yttrium was somewhat more difficult, owing to the presence of potassium and oxalic acid. The oxalic acid was oxidized by boiling the solution with an excess of potassium bromate and nitric acid, and the yttrium was precipitated by ammonium hydroxide. The precipitate was carefully washed with hot water, containing a little ammonium hydroxide and ignited to the oxide. The liquid phases were all analyzed in this manner.

During the analyses of the solid phases it was discovered that this method introduced a slight error, due to the fact that it was impossible to free the precipitated yttrium hydroxide from all bromine. Therefore the per cent. of yttrium as determined in all the liquid phases must be a trifle too high. The error is so slight, however, that it makes no perceptible difference as plotted and, therefore, it was not considered necessary to repeat the analyses. In the case of the solid phases it was found imperative to apply a different method, since the error introduced

[1] THIS JOURNAL, 30, 563.
[2] *Monatsh.*
[3] THIS JOURNAL, 32, 873.

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was much greater than with the liquid phases. It was found by simply igniting a weighed sample of the solid in a tared platinum crucible, treating with water, and washing on a filter, that the potassium and C_2O_3 could be entirely separated, leaving only yttrium oxide. This method gave good results, when carefully tested with samples of known composition, and it was applied in the analyses of the solid phases.

The results of the analyses of the liquid phases are given in Table I and shown graphically in Fig. 1.

TABLE I.

No.	Sp. gr.	Per cent. $Yt_2(C_2O_4)_3$.	Per cent. $K_2C_2O_4$.	Grams $Yt_2(C_2O_4)_3$ per 100 grams H_2O.	Grams $K_2C_2O_4$. per 100 grams H_2O.
1	1.008	Trace	1.29	Trace	1.31
2	1.022	0.01	3.23	0.01	3.34
3	1.035	0.02	5.03	0.02	5.30
4	1.052	0.04	7.04	0.04	7.58
5	1.059	0.06	8.15	0.06	8.88
6	1.081	0.13	10.92	0.15	12.28
7	1.096	0.24	12.63	0.27	14.50
8	1.107	0.33	13.90	0.38	16.20
9	1.132	0.59	16.76	0.72	20.27
10	1.137	0.69	17.64	0.85	21.59
11	1.166	1.08	20.43	1.37	26.02
12	1.173	1.12	21.16	1.45	27.24
13	1.174	1.16	21.28	1.50	27.44
14	1.184	1.14	22.00	1.48	28.63
15	1.199	1.11	24.44	1.49	32.83
16	1.204	1.11	25.09	1.50	33.98
17	1.222	1.06	27.08	1.48	37.68
18	1.231	1.01	27.84	1.42	39.12
19	1.231	0.97	27.84	1.36	39.10
20	1.228	0.78	27.72	1.09	38.77
21	1.218	..	27.47	..	37.87

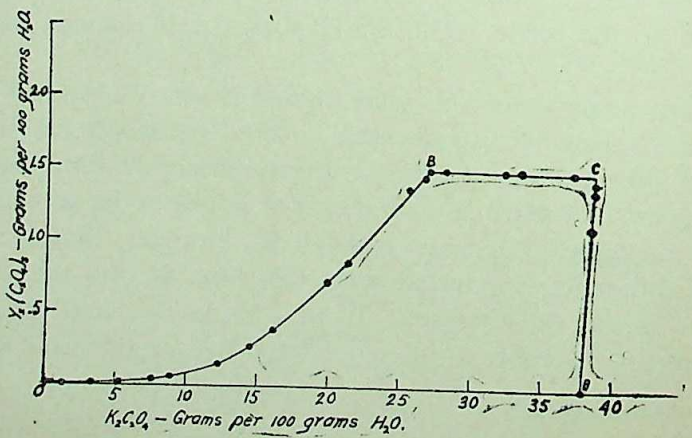


Fig. 1.

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Bottles 18, 19 and 20 contained an excess of potassium oxalate. Bottle 21 contained pure potassium oxalate in excess, for the determination of the solubility.

In the analyses of the solid phases, the samples were withdrawn by means of a platinum spoon and pressed between filter paper in order to remove the adhering mother liquor as far as possible. The sample was then quickly transferred to a weighing bottle and thoroughly mixed. Two portions of this prepared sample were weighed out, and the C_2O_3 and Y_2O_3 determined as previously described.

The data obtained are shown in Table II and plotted in Fig. 2.

TABLE II.

	Liquid.		Solid.	
No.	Per cent. $Y_2(C_2O_3)_4$.	Per cent. $K_2C_2O_4$.	Per cent. $Y_2(C_2O_4)_3$.	Per cent. $K_2C_2O_4$.
1	trace	1.29	48.84	15.79
2	0.01	3.34	45.98	15.44
5	0.06	8.15	46.17	17.64
8	0.33	13.90	44.10	18.75
10	0.69	17.64	45.09	19.49
11	1.08	20.43	42.28	17.88
14	1.14	22.00	29.93	46.56
16	1.11	25.09	31.11	48.01
17	1.06	27.08	31.45	49.14

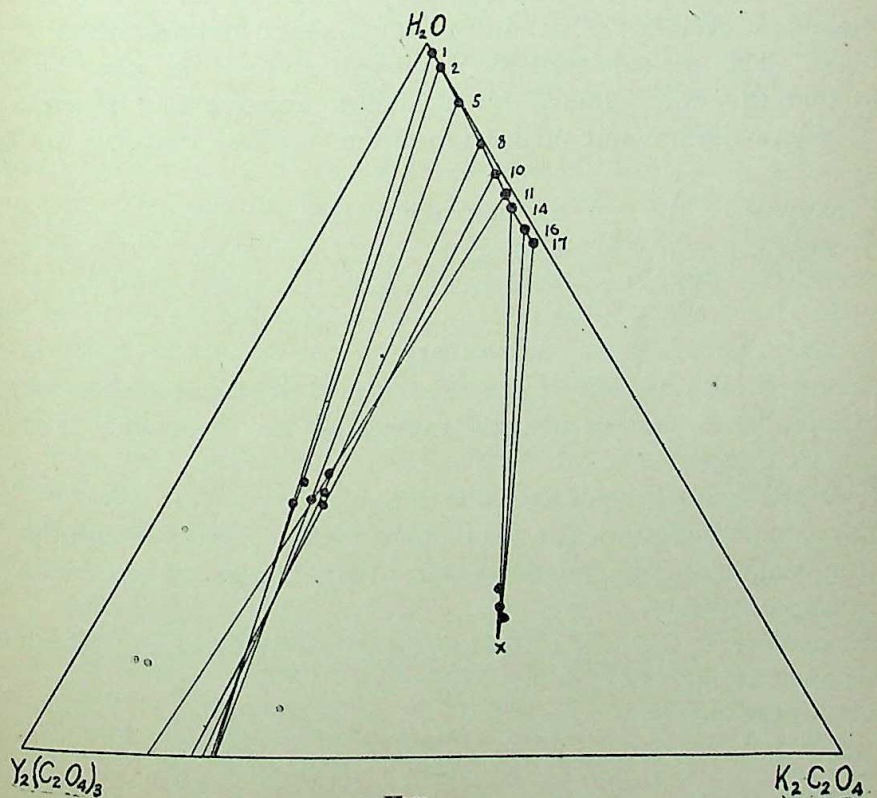


Fig. 2.

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The solubility curve (Fig. 1) shows three distinct parts: AB, BC and CD. In the study of the solid phases along AB (Fig. 1), by means of the triangular diagram (Fig. 2) it is apparent that only solid solutions exist. It is very interesting to note that yttrium oxalate has the power to withdraw a comparatively large amount of potassium oxalate from dilute solutions.

From B to C (Fig. 1) the solid portions were very crystallin, settled readily and had the appearance of a distinct compound. Lines joining points representing liquid and corresponding solid phases along this portion of the curve intersect at the common point X (Fig. 2), corresponding to a definit double oxalate of yttrium and potassium, represented by the formula $Y_2(C_2O_4)_3.4K_2C_2O_4.12H_2O$.

Another interesting fact, shown by the branch CD (Fig. 1), is the increased solubility of potassium oxalate in the presence of yttrium oxalate.

A small quantity of the double oxalate of yttrium and potassium was prepared by dissolving yttrium oxalate in a hot, fairly concentrated solution of potassium oxalate. Upon cooling, the compound crystallized out slowly. The mother liquor was poured off and an attempt was made to free the crystals from the adhering solution. Since the compound is rapidly decomposed by water, it was necessary to find some other solvent to remove the mother liquor. The first method tried was by the use of a solution of ammonium acetate, followed by alcohol to remove the ammonium acetate. This caused only a slight decomposition of the compound. The second method employed glycerol as the washing reagent and this was followed by alcohol to remove the glycerol. By this procedure the amount of decomposition was less than by the first method.

The analyses of the material prepared in this manner are given below:

Calculated	$Y_2(C_2O_4)_3$—33.40, $K_2C_2O_4$—50.24, H_2O—16.36.
Found	$Y_2(C_2O_4)_3$—33.25, $K_2C_2O_4$—49.65, H_2O (diff.) 17.10.
Found	$Y_2(C_2O_4)_3$—33.24, $K_2C_2O_4$—49.63, H_2O (diff.) 17.13.

Summary.

1. The foregoing work shows the existence of only one double oxalate of yttrium and potassium at 25°, possessing the following formula: $Y_2(C_2O_4)_3.4K_2C_2O_4.12H_2O$.

Cleve and Hoeglund mentioned this double salt.[1]

2. This compound can exist in contact with an aqueous solution of potassium oxalate of concentration greater than 27.5 grams of the oxalate to 100 grams of water.

3. The oxalate $Y_2(C_2O_4)_3.K_2C_2O_4.H_2O$, described by Cleve and Hoeglund, does not exist at 25°.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

[1] *Loc. cit.*

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THE RAPID DETERMINATION OF NICKEL AND COBALT BY MEANS OF THE GAUZE CATHODE AND STATIONARY ANODE.

By Raymond C. Benner and William H. Ross.

Received December 12, 1910.

The use of the gauze electrode as a rapid means of depositing several of the elements has recently been made the subject of a number of investigations. From comparative tests made on the use of this cathode when the solution is rotated by magnetic means as devised by Frary[1] and with the gauze cathode alone, Palmer and Palmer[2] arrived at the conclusion that the gauze electrode, rather than the magnetic rotation of the solution, was the main reason for the success of Frary's method and that this would warrant its use as a simple, rapid means of depositing some of the metals. Stoddard arrived at a similar conclusion a short time previous to this. The work of Frary and Peterson,[3] however, does not exactly confirm these results, for, although comparatively favorable results were obtained in depositing copper on the gauze cathode, yet they are of the opinion that mechanical stirring of the electrolyte may not be generally dispensed with. This is borne out by Price and Humphreys,[4] who conclude from a number of determinations made on several different elements, that for rapid electrochemical analysis, stationary electrodes are not as reliable and satisfactory as rotating electrodes or other means of mechanical agitation of the electrolyte.

Most chemists who have studied this means of deposition have made but a few experiments on each metal, endeavoring to cover the entire field and pass upon the method in general without anything like a thorough study of any one element. The very satisfactory results which were obtained by one of us[5] in the determination of copper and lead with the gauze electrode have led the authors to extend the method to several other metals in different electrolytes in order that the true value of this form of electrode as a rapid means of depositing many of the metals might be established.

The reason for the possibility of the utilization of higher currents with the gauze electrode than with other forms of stationary electrodes appears from the recent work of Blasdell and Cruess[6] and from a few experiments which have been carried on by the authors in connection with other work along this line, to be due to the fact that this form of electrode allows the free circulation of the electrolyte, caused by means of the convection currents set up by the process of electrolysis.

[1] *Z. Elektrochem.*, 23, 308.
[2] *Trans. Am. Elektrochem. Soc.*, 15, 489 (1909).
[3] May Meeting (1910) American Electrochemical Society.
[4] *J. Soc. Chem. Ind.*, 29, 307.
[5] Benner, *J. Ind. Eng. Chem.*, 2, 195, 348.
[6] This Journal, 32, 1264.

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Nickel.

Stoddard[1] and Price and Humphreys[1] have each made a few depositions of this element from an ammonium hydroxide solution containing ammonium sulfate in a manner similar to that which we have adopted but did not extend their investigation of this element to include other electrolytes.

In order that a thorough study might be made of the deposition of nickel, a solution of the sulfate was prepared and the nickel content of 10 cc. determined by precipitation with sodium hydroxide and bromine water. The oxide obtained on ignition was reduced to the metal which weighed 0.1808 gram as the mean of five closely agreeing determinations. The nickel content of this solution was also determined by means of the ordinary electrolytic method from an ammonium sulfate electrolyte strongly alkaline with ammonia. The mean of five determinations amounted to 0.1811 gram. The average of the two gave 0.18095 gram as the nickel contained in 10 cc. of the solution.

A second solution used in determining rates of precipitation was standardized electrolytically and found to contain 0.1851 gram of nickel in 10 cc. of the solution.

With these solutions as standards a great many determinations were made for the purpose of comparing the efficiency of the gauze electrode as a means of depositing this metal from the different electrolytes commonly used in the old electrolytic methods. A number of determinations were likewise made in ammonium carbonate solution, concerning which we have been able to find no reference to its use as an electrolyte in the literature. It proved a most satisfactory solution from which to deposit both cobalt and nickel.

The gauze cathodes used in these experiments were cylindrical in shape but of two sizes. The smaller sized cathodes were about 6 grams in weight and made of platinum wire 0.1 mm. in diameter with 26 meshes to the cm. They were 3.5 cm. high by 2.5 cm. in diameter. The corresponding dimensions of the large cathode were 4 cm. by 3.5 cm. and it was made of platinum wire 0.2 mm. in diameter with 18 meshes to the cm. This difference in the size of the cathodes had but little effect on the character of the deposits obtained.

Ammonium Sulfate Electrolyte.—This electrolyte, consisting of ammonium sulfate in ammoniacal solution, is perhaps more commonly used than any other of the older electrolytes. With the gauze electrode the nickel deposited from this electrolyte was almost the color of platinum, very adherent and satisfactory in every respect. In addition to this, the convenience with which the electrolyte can be used makes it one of the most desirable for the determination of this metal. It was not found

[1] *Loc. cit.*

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possible to precipitate nickel from this electrolyte containing much excess of a mineral acid. When the solution was neutral, or slightly ammoniacal, there was a tendency for a deposit to form on the anode. This was entirely prevented by the use of ammonia as directed in the following table, which shows the conditions under which successful determinations were made. When a smaller amount of ammonia is used anodic deposition may be prevented by the addition of glycerol mixture as used by E. F. Smith (5 cc. glycerol, 45 cc. alcohol and 50 cc. water) but this was not found to be as effective as the use of ammonia. It was used, however, in those determinations marked with an asterisk.

Amount taken.	Amount found.	Error. mg.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonium sulfate. grams.	Ammonia, sp. gr. 0.91. cc.	
0.1810	0.1807	—0.3	3	4–5	25	35	3	10	
0.1810	0.1809	—0.1	3	4–5	25	35	3	10	
0.3619	0.3627	+0.8	3	5–6	25	60	3	10	
0.1810	0.1804	—0.6	3	4–5	25	35	3	5	deposit on anode.
0.3619	0.3617	—0.2	3	5–6	20	60	3	10	
0.1810	0.1810	±0.0	3	4–5	25	35	3	5*	no deposit
0.1810	0.1813	+0.3	4	5–6	20	60	3	5*	on anode.
				Rate of precipitation.					
0.1851	0.0833		4	5	2	35	3	10	
0.1851	0.1307		4	5	4	35	3	10	
0.1851	0.1640		4	5	6	35	3	10	
0.1851	0.1836		4	5	12	35	3	10	
0.1851	0.1850		4	5	15	35	3	10	
0.1851	0.1851		4	5	20	35	3	10	

From the rate of precipitation it is seen that it is possible to precipitate 0.1851 gram of nickel in 15 minutes. In this set of experiments as well as in those following, the metal was shown to be completely precipitated in the time given, by careful qualitative tests with ammonium sulfide.

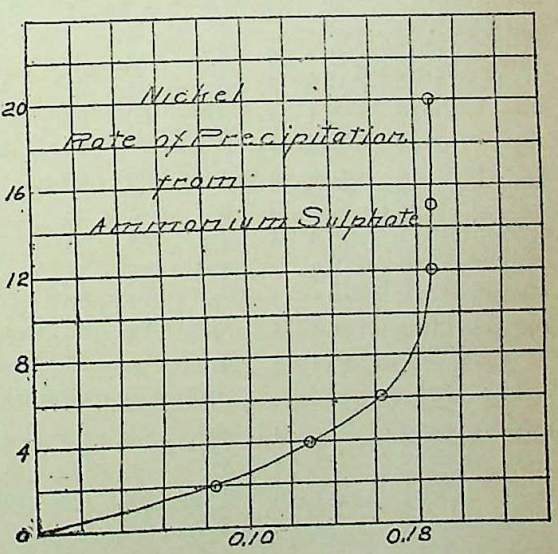


Fig. 1.

Ammonium Acetate Electrolyte. — This electrolyte gave good results under the conditions shown in the table when an excess of ammonia was used. Solutions which contained a slight excess of acetic acid at the be-

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ginning of the electrolysis gave good deposits which could scarcely be distinguished in color from the platinum but it was observed that the electrolyte became alkaline as the deposition of the metal proceeded. When enough acid was added to keep the electrolyte acid to the end of the electrolysis the precipitation was either greatly delayed or not complete, and likewise, there was a tendency to anodic deposition. In ammoniacal solution the deposit on the anode can be prevented by the use of sufficient ammonia, or glycerol mixture, as in case of the ammonium sulfate electrolyte. The results tabulated below show that it is possible to precipitate 0.3706 gram of nickel in 20 minutes and likewise the conditions under which good deposits and quantitative results may be expected.

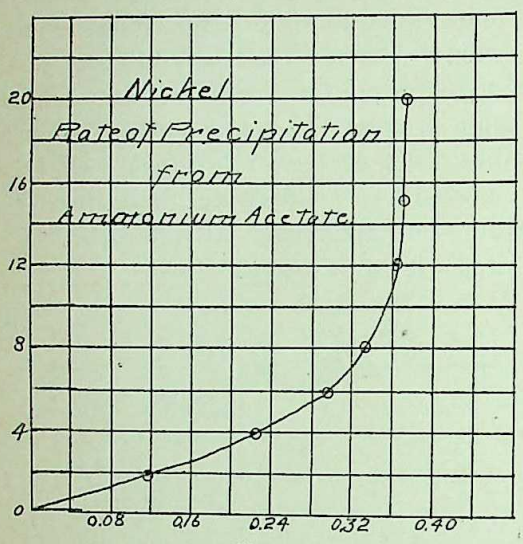


Fig. 2.

Amount taken.	Amount found.	Error	Amperes.	Volts.	Time, Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Acetic acid, 80 per cent. cc.	
0.1810	0.1813	+0.3	3	4–5	25	35	15	5	
0.1810	0.1816	+0.6	3	4–5	25	35	15	5	
0.3619	0.3618	—0.1	4	5–6	20	60	15	5	
0.3619	0.3624	+0.5	4	5–6	20	60	15	5	
0.3619	0.3625	+0.6	4	5–6	20	60	15	5	
0.1810	0.1801	—0.8	3	4–5	25	35	20	10	
0.1810	0.1813	+0.3	3	4–5	25	35	2	slightly acid with acetic acid*	
0.1810	0.1816	+0.6	3	4–5	25	35	2	slightly acid with acetic acid*	
0.1810	0.1811	+0.1	3	5	25	60	2	slightly acid with acetic acid*	
0.3619	0.3623	+0.4	3	5	25	60	2	slightly acid with acetic acid*	
0.1810	0.1808	+0.2	3	4–5	15	35	2	slightly acid with acetic acid*	
				Rate of precipitation.					
0.3702	0.1159		4	5–6	2	60	15	5	
0.3702	0.2231		4	5–6	4	60	15	5	
0.3702	0.3337		4	5–6	8	60	15	5	
0.3702	0.3630		4	5–6	12	60	15	5	
0.3702	0.3659		4	5–6	15	60	15	5	
0.3702	0.3706		4	5–6	20	60	15	5	
0.3702	0.3706		4	5–6	25	60	15	5	

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Sodium Acetate Electrolyte.—The deposition of nickel from a solution of sodium acetate containing free acetic acid was quite satisfactory. The deposits had the color of platinum and were perfectly adherent. The electrolyte became alkaline when a neutral or very slightly acid solution was used but unlike the results obtained with the ammonium acetate electrolyte it was found that the deposition of the metal from a solution which remained acid to the end of the electrolysis was only slightly retarded. Glycerol mixture was used to prevent anodic deposition.

Amount taken.	Amount found.	Error.	Amperes	Volts.	Time. Minutes.	Volume of solution. cc.	Sodium acetate. Grams.	Acetic acid, 80 per cent. cc.
0.1810	0.1816	+0.6	3	6–7	30	35	2	2*
0.1810	0.1814	+0.4	3	6–7	35	35	2	2*
0.1810	0.1815	+0.5	3	6–7	35	35	2	2*
0.1810	0.1816	+0.6	3	6–7	30	35	2	1.5*
0.1851	0.1856	+0.5	3	6–7	30	35	2	2*
0.3702	0.3707	+0.5	3	6–7	30	35	2	2*

Ammonium and Sodium Formate Electrolytes.—The deposition of nickel from ammonium formate in alkaline solution, and sodium formate in both acid and alkaline solutions has been tried with results similar to those obtained with ammonium and sodium acetate under corresponding conditions.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia sp. gr. 0.91. cc.	Formic acid. 1.06 sp. gr. cc.
0.1810	0.1811	+0.1	3	5–6	25	60	2	slight excess*
0.1810	0.1806	—0.4	3	4–5	30	35	15	5
0.1810	0.1808	—0.2	3	4–5	30	35	15	5
0.3619	0.3621	+0.2	3	4–5	30	35	15	5
0.3619	0.3624	+0.5	4	5–6	30	60	15	5
0.3619	0.3618	—0.1	4	5–6	20	60	15	5
0.1810	0.1814	+0.4	4	4–5	20	35	15	5
							Sodium carbonate, gram.	
0.1810	0.1807	—0.3	3	6–7	30	60	1	2 excess*
0.1810	0.1811	+0.1	3	6–7	30	60	1	2 excess*
0.1810	0.1803	—0.7	4	6–7	30	60	1	2 excess*
0.1810	0.1806	—0.4	3	5–6	30	35	1	2 excess*
0.1810	0.1815	+0.5	3	5–6	30	35	2	2 excess*
0.1810	0.1813	+0.3	3	5–6	35	35	2	2 excess*
0.1810	0.1815	+0.5	3	5–6	25	35	2	2 excess*

Ammonium Carbonate Electrolyte.—The results obtained from a solution of ammonium carbonate were usually a little too high. By adding a few cc. of ammonium hydroxide the high results were prevented and excellent deposits obtained in all cases.

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Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonium carbonate. Grams.	Ammonia, sp. gr. 0.91. cc.
0.1851	0.1851	±0.0	4	5–6	20	35	4	10
0.1851	0.1853	+0.2	4	5–6	20	35	4	10
0.1851	0.1857	+0.6	4	5–6	20	35	4	5
0.1851	0.1850	—0.1	4	5–6	20	35	4	5
0.3620	0.3624	+0.4	4	5–6	20	60	4	10
0.3620	0.3630	+1.0	4	5–6	20	60	4	10
			Rate of precipitation.					
0.1851	0.0825		4	5–6	2	35	4	5
0.1851	0.1430		4	5–6	4	35	4	5
0.1851	0.1681		4	5–6	6	35	4	5
0.1851	0.1803		4	5–6	8	35	4	5
0.1851	0.1823		4	5–6	10	35	4	5
0.1851	0.1846		4	5–6	12	35	4	5
0.1851	0.1855		4	5–6	20	35	4	5

Ammonium Oxalate Electrolyte.—Nickel can be deposited from a solution of ammonium oxalate containing a slight excess of mineral acid, from a neutral solution and also from a solution alkaline with ammonium hydroxide. The results obtained from neutral and acid solutions were nearly always high, probably due to the deposition of carbon. In alkaline solutions this was not quite so marked. The deposits were bright in color and perfectly adherent. Because of its comparatively low solubility, this electrolyte, however, is not as convenient to use as some of the others.

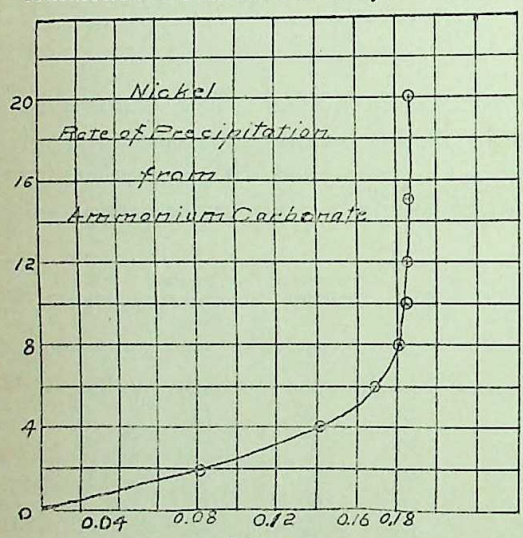


Fig. 3.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonium oxalate. Grams.	Ammonia, sp. gr. 0.91. cc.
0.1810	0.1805	—0.5	4	5–6	25	60	3	10
0.1810	0.1812	+0.2	3	4–5	25	30	3	10
0.3620	0.3629	+0.9	4	5–6	20	60	4	5
0.3620	0.3623	+0.3	4	5–6	20	60	4	5
0.1851	0.1847	—0.4	4	5–6	20	60	4	5
0.1810	0.1819	+0.9	4	4–5	20	30	4	10
0.1810	0.1823	+1.3	4	4–5	20	30	4	10
0.1810	0.1817	+0.7	4	4–5	20	30	4	10

Potassium Cyanide Electrolyte.—A number of careful experiments were made with potassium cyanide as an electrolyte but satisfactory results

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could not be obtained with the high currents used. When preparing this electrolyte a dilute solution of potassium cyanide was carefully added to the nickel solution, from a buret, drop by drop, until the precipitate, which first formed, redissolved. A few drops were then added in excess. As the electrolysis proceeded the cyanide was decomposed with the result that nickel was precipitated.

Cobalt.

The rapid deposition of cobalt has not been made so far by means of the gauze cathode, with stationary anode. The solution of cobalt sulfate used in the following experiments was standardized first by the old electrolytic method from an electrolyte containing ammonia and ammonium sulfate. As a mean of five closely agreeing determinations, 10 cc. of the solution were found to contain 0.1052 gram of cobalt. When the solution was made acid with sulfuric acid, evaporated and weighed as the sulfate, the residue corresponded to 0.1050 gram of cobalt. This gave 0.1051 gram as the mean of the two methods for the nickel content of the solution.

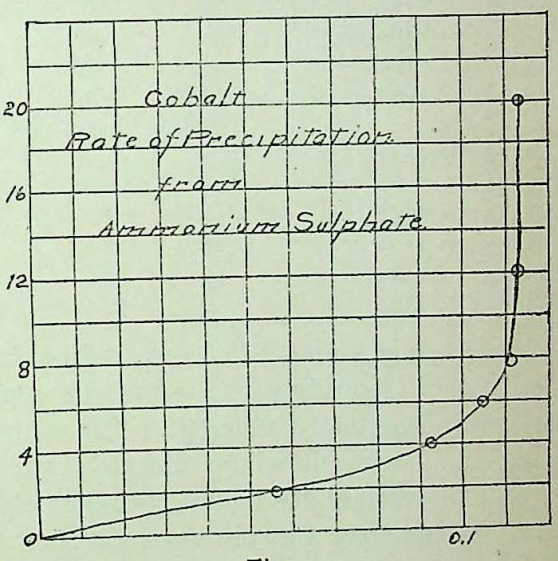


Fig. 4.

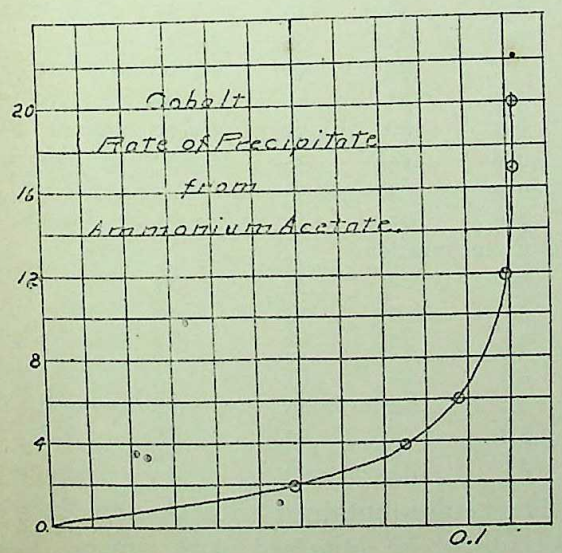


Fig. 5.

Ammonium Sulfate Electrolyte.—The use of this electrolyte in the rapid precipitation of cobalt gave as satisfactory results as were obtained in case of nickel in neutral or slightly alkaline solutions. Cobalt had a tendency to form deposits on the anode. This, however, was not as marked as in case of nickel and could be prevented in a similar manner, by the use of glycerol mixture or by the addition of strong ammonia. The deposits obtained were dark colored

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but perfectly adherent and in every way satisfactory. As shown in the table complete precipitation could be made in 15 minutes from a solution containing 0.1125 gram of cobalt.

Amount taken	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Ammonium sulphate. Grams
0.2102	0.2102	±0.0	3–4	5–6	30	65	10	6
0.2102	0.2108	+0.6	3–4	5–6	30	65	10	6
0.1051	0.1055	+0.4	4–5	5–6	20	35	10	3
0.1051	0.1052	+0.1	4–5	5–6	20	35	10	3
0.2102	0.2101	—0.1	7	6–8	18	40	10	3
0.2102	0.2104	+0.2	7	6–8	18	40	10	3
0.2102	0.2104	+0.2	6–7	6–8	20	65	10	3
0.1051	0.1050	—0.1	5–6	6–7	20	35	10	3
			Rate of precipitation.					
0.1125	0.0547		4	6	2	35	10	3
0.1125	0.0968		4	6	4	35	10	3
0.1125	0.1048		4	6	6	35	10	3
0.1125	0.1109		4	6	8	35	10	3
0.1125	0.1122		4	6	12	35	10	3
0.1125	0.1120		4	6	20	35	10	3

Ammonium Acetate Electrolyte.—Ammonium acetate was not only a very convenient electrolyte to use but the deposits obtained were moderately bright and perfectly adherent. The same results were obtained in acid solution as were noted for nickel. In this as well as in the ammonium sulfate electrolyte the tendency of the cobalt to deposit on the anode was less marked than was observed in the case of nickel and did not occur under the conditions given in the table.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Acetic acid, 80 per cent. cc.
0.1051	0.1050	—0.1	4–5	5–6	30	35	15	5
0.1051	0.1047	—0.4	4–5	5–6	30	35	15	5
0.2102	0.2100	—0.2	4–5	6–7	35	60	20	10
0.1051	0.1055	+0.4	3–4	4–5	35	40	20	10
0.2102	0.2100	—0.2	4–5	6–7	20	60	20	10
0.1051	0.1045	—0.6	3–4	4–5	25	35	15	5
0.1051	0.1055	+0.4	3–4	4–5	25	35	5	5*
0.1051	0.1048	—0.3	3–4	4–5	25	35	5	5*
			Rate of precipitation.					
0.1125	0.0594		4	5	2	35	15	5
0.1125	0.0848		4	5	4	35	15	5
0.1125	0.0978		4	5	6	35	15	5
0.1125	0.1096		4	5	12	35	15	5
0.1125	0.1111		4	5	17	35	15	5
0.1125	0.1125		4	5	20	35	15	5
0.1125	0.1127		4	5	25	35	15	5

Sodium Acetate Electrolyte.—The results obtained with this electrolyte were comparable in all respects to those obtained with nickel. The deposits formed in acid solutions were brighter than those obtained in

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ammoniacal solution. The retarding effect of different amounts of acid may be seen by referring to the table.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time Minutes.	Volume of solution. cc.	Sodium acetate. Grams.	Acetic acid, 80 per cent. cc.
0.1125	0.1127	+0.2	3	6–8	30	35	2	1.5
0.1125	0.1125	0.0	3	6–8	35	35	2	2.0
0.1125	0.1129	+0.4	3	6–8	35	35	2	1.5
0.1125	0.1127	+0.2	3	6–8	25	35	2	1.5
0.1125	0.1121	—0.4	3	6–8	30	35	2	2.0
0.1125	0.1127	+0.2	3	6–8	25	35	2	1.5
0.2250	0.2190		3	7	15	35	2	1.0
0.2250	0.2111		3	7	15	25	2	2.0
0.2250	0.1995		3	7	15	25	2	3.0
0.2250	0.1825		3	7	15	35	2	5.0
0.2250	0.1629		3	7	15	35	2	10.0
				Rate of precipitation.				
0.2250	0.0572		3	7	2	35	2	3
0.2250	0.0982		3	7	4	35	2	3
0.2250	0.1176		3	7	6	35	2	3
0.2250	0.1434		3	7	8	35	2	3
0.2250	0.1823		3	7	12	35	2	3
0.2250	0.2130		3	7	20	35	2	3
0.2250	0.2235		3	7	25	35	2	3
0.2250	0.2243		3	7	30	35	2	3
0.2250	0.2245		3	7	40	35	2	3

Sodium and Ammonium Formate Electrolyte.—These electrolytes gave good results, under the same conditions as have already been described in the use of the sodium and ammonium acetate electrolytes.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Formic acid, sp. gr. 1.06. cc.
0.1051	0.1051	±0.0	4	5–6	20	35	15	5
0.2102	0.2095	—0.7	4	5–6	20	35	15	5
0.2102	0.2110	+0.8	4	5–6	25	35	7	5*
0.1051	0.1055	+0.4	3–4	5–6	25	35	7	5*
0.1051	0.1056	+0.5	3–4	5–6	25	35	7	5*
0.1051	0.1059	+0.8	3–4	5–6	25	35	7	5*
				Rate of precipitation.				
0.2250	0.0911		4	5–6	2	35	10	5
0.2250	0.1544		4	5–6	4	35	10	5
0.2250	0.1942		4	5–6	6	35	10	5
0.2250	0.2142		4	5–6	8	35	10	5
0.2250	0.2229		4	5–6	12	35	10	5
0.2250	0.2236		4	5–6	15	35	10	5
0.2250	0.2247		4	5–6	20	35	10	5
							Sodium carbonate. Grams.	
0.1125	0.1123	—0.2	3	6–7	35	35	2	2 excess*
0.1125	0.1126	+0.1	3	6–7	35	35	2	2 excess*
0.1125	0.1124	—0.1	3	6–7	35	35	2	2 excess*
0.1125	0.1124	—0.1	3	6–7	35	35	1	3 excess*
0.2250	0.2240	—1.0	3	6–7	35	35	1	3 excess*

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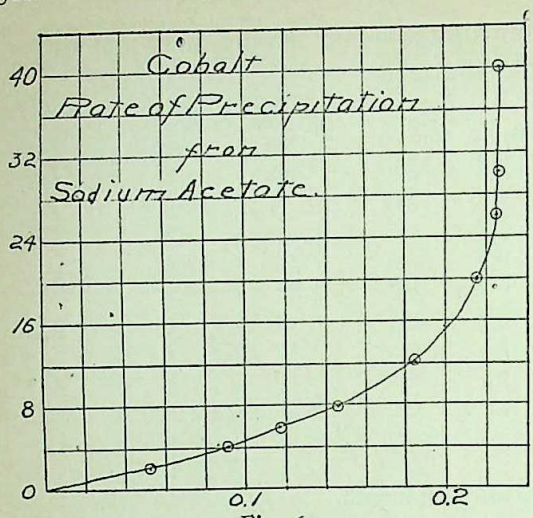


Fig. 6.

Ammonium Carbonate Electrolyte.—The precipitation of cobalt from this new electrolyte was attended with uniform success. The deposits were invariably good and there was no tendency to anodic deposition either with or without the addition of ammonia to the solution. This fact makes this electrolyte one of the most satisfactory which we have used. As the standard cobalt solution was slightly acid, an excess of ammonia was usually added before the carbonate to prevent loss by effervescence.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Ammonium carbonate. Grams.
0.1051	0.1055	+0.4	3–5	5–6	25	35	5	5
0.1051	0.1052	+0.1	3–5	5–6	25	35	5	5
0.1051	0.1054	+0.3	3–5	5–6	23	35	5	5
0.1051	0.1052	+0.1	3–5	5–6	23	35	5	4
0.2102	0.2096	—0.6	3–5	5–6	25	35	5	6
0.2102	0.2096	—0.6	3–5	5–6	25	35	5	6
0.1051	0.1049	—0.2	4	5–6	20	35	5	4
0.1051	0.1056	+0.5	4	5–6	20	35	5	4
			Rate of precipitation					
0.1125	0.0594		4	5–6	2	35	5	5
0.1125	0.0908		4	5–6	4	35	5	5
0.1125	0.1054		4	5–6	6	35	5	5
0.1125	0.1092		4	5–6	8	35	5	5
0.1125	0.1119		4	5–6	10	35	5	5
0.1125	0.1125		4	5–6	15	35	5	5
0.1125	0.1123		4	5–6	20	35	5	5

Ammonium Oxalate Electrolyte.—The results with ammonium oxalate, which is a standard electrolyte in the older electrolytic methods, were usually a little low. This held true whether the solution was slightly acid with a mineral acid, neutral or alkaline with ammonia. This was found to be due to a small amount of the cobalt being precipitated during the electrolysis, and which was not redissolved during the time usually allowed for the determination. This result, together with the fact that the ammonium oxalate can not be as conveniently used as the other electrolytes, because of its low solubility, makes it an electrolyte which cannot be recommended for the rapid determination of cobalt on the gauze electrode.

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Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc	Ammonium oxalate. Grams.
0.1051	0.1051	±0.0	4–5	6–7	20	35	....	4
0.1051	0.1051	±0.0	4–5	6–7	20	35	....	4
0.1051	0.1041	—1.0	4–5	6–7	20	35	....	4
0.1051	0.1046	—0.5	4–5	6–7	20	35	....	4
0.1051	0.1043	—0.8	3–5	5–6	20	35	5	3
0.1051	0.1045	—0.6	3–5	5–6	20	35	5	3

Potassium Cyanide Electrolyte.—The same negative results were obtained in the deposition of cobalt with this electrolyte as were noted for nickel.

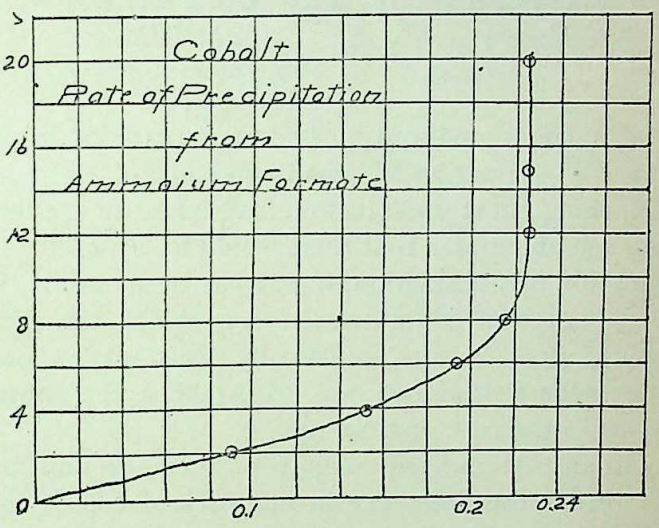


Fig. 7.

Conclusion.

1. The rapid determination of nickel and cobalt by means of the gauze electrode and stationary anode is perfectly satisfactory with most of the electrolytes in common use.

2. The rate at which they are precipitated is practically the same for all of the electrolytes which can be used in ammoniacal solution and is little affected by the amount of ammonia added. In acid solution the rate of precipitation is not quite as great as in ammoniacal solution and decreases slightly as the amount of acid is increased.

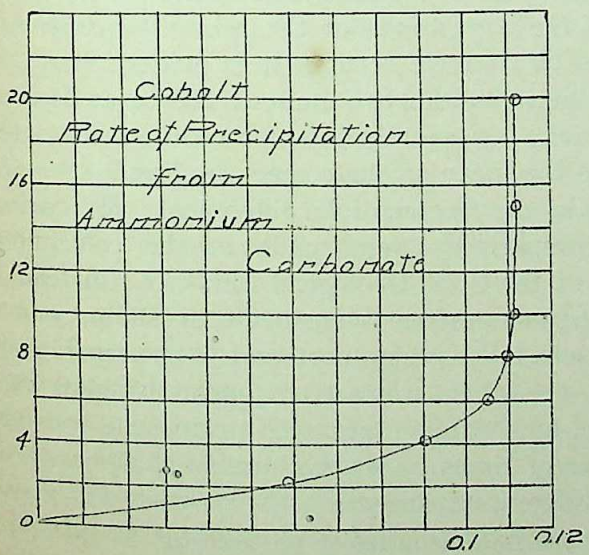


Fig. 8.

3. Although the rate of precipitation of these elements on the gauze electrode is not quite equal to the rate at which they are precipitated by means of the same current when the electrolysis is agitated by mechanical means, it is rapid

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enough for practical purposes and much more satisfactory on account of the simplicity of the apparatus and the fact, that, when desired, the older methods with small currents may be used with the same electrode, and without alteration of the rest of the apparatus.

UNIVERSITY OF ARIZONA,
TUCSON.

SENSITIVENESS OF THE COLORIMETRIC ESTIMATION OF TITANIUM.[1]

BY ROGER C. WELLS.

Received January 27, 1911.

The color produced by hydrogen peroxide in titanium solutions serves for the estimation of small amounts of titanium and also, through a bleaching effect upon it, for small quantities of fluorine. At first thought one might suppose that there would be a concentration of maximum accuracy for this estimation, but it has been shown that there is in general a wide range of concentration over which the accuracy of a colorimetric comparison remains practically constant.[2] The object of the experiments here described was to establish the range of suitable concentrations in the case of titanium.

In any colorimetric comparison there is a limit to the difference of shade, or rather the difference in intensity of color, which the eye can detect. One may prepare two known solutions, one of which will be just perceptibly stronger in color, the other just perceptibly weaker than a given unknown solution. The difference in concentration of the two extremes, divided by 2, will be a certain *fraction* of the mean total substance present, and this fraction, expressed as a percentage, may be said to represent the maximum error of the comparison, or the *perceptible difference*. In comparing two solutions by a single setting, it is evident that the setting may fall anywhere between the two limits. Hence an average of several readings is essential. An equally good procedure is to determin the two limits and take the mean as the correct reading.

It was sought to determin the "perceptible differences" for various titanium solutions. The comparisons were made in the colorimeter devised by George Steiger, of the U. S. Geological Survey.[3] Instead of preparing many solutions the comparisons were made by sliding one of the cells. Scale distances were taken as proportional to concentrations. One cell was set to read 10, the other was set to appear either stronger or weaker as the case might be. After alternately resting the eyes and observing the cells a number of times, when a plurality of observations indicated that there was a difference in intensity, the position was noted.

[1] Published by permission of the Director of the U. S. Geological Survey.
[2] D. W. Horn and Sue A. Blake, *Am. Chem. J.*, 36, 202 (1906).
[3] THIS JOURNAL, 30, 215 (1908).

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If no difference was perceptible a new setting was made and tried in the same way. The judgment is noticeably better immediately after resting the eyes. The difference in the two final settings, one stronger, the other weaker than the reference solution, divided by 20, gives the "perceptible differences" of the comparison. Division by 2 is made because the perceptible difference was doubly determined, and by 10 because the scale readings were made in a layer of 10 cm. This percentage error or limit of perception will then apply to any given titanium determination, whatever may be the volume of the solution. The solutions contained about 3 per cent. of sulfuric acid and 2 per cent. of "dioxygen."

PEROXIDIZED TITANIUM SULFATE.

Expt.	Concentration Mg. TiO_2. in 100 cc.	Color.	Reading on cell stronger than reference.	Reading on cell weaker than reference.	Perceptible difference. Per cent.
1	0.30	Very slight	8.7	11.8	15.
2	0.63	Pale straw	7.5	10.5	15.
3	1.0	Pale straw	10.0	11.1	7.5
4	1.3	Straw	9.3	12.0	14.
5	1.6	Straw	10.0	11.3	6.5
6	1.6	Straw	9.8	11.0	6.0
7	2.5	Lemon-yellow	9.2	10.7	7.5
8	4.0	Lemon-yellow	9.3	10.5	6.0
9	5.0	Yellow	9.2	10.8	8.0
10	8.4	Yellow	9.3	10.5	6.0
11	10.0	Yellow	8.8	10.3	7.5
12	11.2	Yellow	9.7	10.8	5.5
13	15.0	Yellow	9.7	10.8	5.5
14	20.0	Orange-red	9.4	10.8	7.0
15	20.0	Orange-red	9.8	10.9	5.5

Solutions stronger than the last in the table are not suitable for the estimation of titanium by colorimetry. It appears that the accuracy of the comparison is practically constant for concentration ranging from 1.5 to 20 mg. TiO_2 in 100 cc., but falls off noticeably in weaker solutions. In the latter a fair comparison can still be obtained by using a larger layer of liquid. The fraction 6.5 per cent. expresses the difference in concentration between two solutions with a just perceptible difference in intensity, as viewed in the colorimeter described. Although this percentage will vary somewhat for different observers and even for the same observer at different times, the range of suitable concentration will average about the same for the majority of persons. In any case the experiments show that the accuracy is practically constant over a wide range.

A determination of titanium by colorimetry may be made much more accurately than the above *perceptible difference*. In the first place any constant error in the colorimeter may be eliminated by the principle of comparing by substitution, that is, by substituting an unknown for a known solution in *one* of the cells, referring each to the same reference

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solution in the other cell. Then one may take the mean of the extreme limits, or of a large number of settings for apparent equality. In one case the method of extreme limits gave 9.8 and 10.9, the mean being 10.35 and ten matchings gave a mean of 10.30, the extremes being 9.9 and 11.4. Determinations of five unknown solutions, comparing by substitution and making 10 settings in each comparison, gave the following results.

Taken.	Found.	Error. Per cent.
10.13	10.26	+1.3
10.46	10.52	+0.7
10.73	10.45	—2.8
10.79	10.71	—0.8
11.17	11.01	—1.6

It therefore seems safe to conclude that titanium may be determined by colorimetry to about 2 per cent. This is a very fortunate circumstance for it enables one to determin titanium quickly in mixtures containing columbium, tantalum, zirconium, tin or other elements whose chemical separation is a lengthy, if not imperfect, procedure.

It is interesting to compare the above results with those obtained by Horn and Blake with chromate and copper solutions, using Nessler tubes.[1] Some of their results are given here, in a form slightly recalculated to show the "perceptible difference" as used above.

Potassium Chromate.

Expt.	Concentration Mg. Cr in 50 cc.	Perceptible difference in mg.	Perceptible difference in per cent.
1	10.5	3.98	38.
3	3.9	0.39	10.
4	2.6	0.18	7.
5	1.3	0.07	5.
7	0.65	0.002	0.3
9	0.26	0.005	2.
11	0.16	0.011	7.
13	0.08	0.0007	0.9
15	0.017	0.008	47.

Copper Sulphate

Expt.	Concentration Mg. Cu in 50 cc.	Perceptible difference in mg.	Perceptible difference in per cent.
1	1930.	154.	8.
3	130.	12.4	10.
5	69.5	5.4	8.
7	57.2	5.8	10.
9	45.8	4.6	10.
11	37.1	3.9	11.
13	30.9	3.1	10.
15	19.3	1.2	6.3
17	9.7	1.7	18.

[1] *Loc. cit.*, pp. 196 and 200.

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These investigators consider that Expt. 4 with chromium and Expt. 5 with copper fall in the range of concentration where the accuracy is constant and a maximum. The normal perceptible difference for chromium is therefore about 7 per cent. and for copper 8 per cent. This appears to be almost the same as for titanium, 6.5 per cent.

Summary.

The accuracy of the colorimetric estimation of titanium is practically constant over concentrations ranging from the strongest down to those containing about 1.5 mg. TiO_2 in 100 cc. The change in concentration required to produce a perceptible difference in intensity between two solutions, at favorable concentrations, was found to be about 6.5 per cent. which does not differ much from the results of others with chromium and copper solutions. With suitable precautions, such as comparing by substitution and taking the mean of several settings or of the two perceptibly different extremes, the accuracy of the colorimetric comparisons appears to be about 2 per cent.

WASHINGTON, LABORATORY OF THE U. S. GEOLOGICAL SURVEY.

[DIVISION OF CHEMISTRY, HYGIENIC LABORATORY, UNITED STATES PUBLIC HEALTH AND MARINE-HOSPITAL SERVICE.]

A CRUCIBLE FURNACE.

BY NORMAN ROBERTS AND F. ALEX. MCDERMOTT.

Received February 1, 1911.

The chief feature of this furnace consists in the replacement of the greater part of the usual solid clay or earthenware wall by an equal or greater thickness of a non-conducting refractory powder, such as light magnesia, kaolin, or even sifted ashes. As compared with a furnace having solid walls composed of clay or some similar substance, the furnace is lighter, cheaper in construction, quicker in heating, and better insulated—hence, it gives a higher temperature and is more economical as to fuel—and wear or damage of any kind is much more circumscribed and accessible and much more easily and cheaply repaired. The insulating layer can be made as thick as desired, with corresponding reduction in the leakage of heat, especially in the region of highest temperature, whereas the practicable thickness of a clay wall is sharply limited by the tendency to crack on change of temperature common to all large masses of poor heat conductors.

This furnace has so far been constructed only in the form of a small gas-fired crucible furnace, with the flame entering at the bottom. In its simplest form it can be improvised in a few minutes from the commonest and most worthless of waste materials. A large cylindrical ether or oil can serves for the outer container; a shovelful of sifted hard-coal

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ashes, for the insulator; and a bottomless tin can, or a sheet of iron (black, tinned or galvanized) rolled into a cylinder, or a short length of cylindrical iron rain spout or stove pipe, for the inner lining. For a more durable form the inner lining may be a cylinder of clay, graphite, etc., but for all temperatures below the melting point of iron, the sheet iron lining is most satisfactory, inasmuch as it can be replaced in a few seconds and at an infinitesimal cost when it burns out, can be handled with absolutely no danger of breaking, and heats up much faster than any more expensive and more massive lining.

The crucible is supported on a triangle of fireclay pipestems of uniform diameter, strung on a single piece of thick iron wire, the wire exposed at the bends being protected by asbestos paste or wrappings of asbestos twine. The triangle is supported on top of a short roll of sheet iron or a clay or iron cylinder (a short length of iron pipe of sufficient diameter will do) which rests on the bottom of the outer container (see Fig. 1).

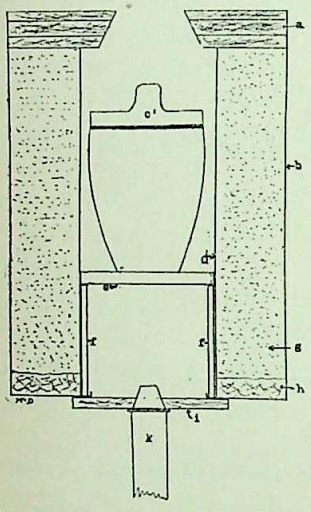


Fig. 1.—Simple form of furnace.

a, Cover, or lid, made of three sheets of asbestos board interspaced with thin sheet iron; *b*, outer container (tin can); *c*, crucible and *c'*, crucible cover; *d*, sheet iron lining (inner container); *e*, supporting triangle for crucible; *f*, iron ring supporting triangle, and resting on bottom of furnace; *g*, powder lining (insulator); *h*, asbestos mat at bottom of outer container; *i*, movable bottom, mounted on nozzle of burner; *k*, nozzle of Fletcher blast lamp.

The lid may be made merely of a circular disk of sheet iron, with a hole in the center, or it may be made of asbestos-board, or of several layers of asbestos-board reinforced with thin sheet iron, or of clay.

It is of advantage to cover the bottom of the outer container inside, under the powder insulation, with a layer of loose asbestos, to prevent the powder leaking out where the joints may not be tight.

The burner may be an ordinary Bunsen, a Teclu, or a blast lamp. In any case the burner supports a movable bottom which partially or entirely closes the bottom of the central tube (inner container). With the blast lamp this bottom is a disk of thick asbestos board, backed with sheet iron, with a hole in the center fitting closely around and sitting firmly on the conical nozzle of the lamp (Fletcher's compound No. 20), and approximated closely to the bottom of the outer container so as to exclude all air except that furnished by the blast. The natural-draft burners need additional air from outside, and hence with them the disk is mounted on a sliding tube provided with a set-screw, so that the whole

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may be moved up and down by burner tube, thus increasing or decreasing the amount of outside air drawn into the furnace.

In case the furnace is to be worked at a temperature approaching the melting point of iron, the lining and crucible support must be of more refractory construction. To this end the lining may be improvised of two graphite crucibles placed vertically bottom to bottom, a large hole being cut through both bottoms. This makes a "corset-shaped" chamber, the upper compartment being large for the crucible containing the material being heated, and the lower compartment being smaller for the flame. Just above the "waist" three projecting knobs (*a*, Fig. 2) of graphite, 120° apart in a horizontal circle, are set into the walls at such a point as to hold the bottom of the crucible well above the "waist," and leave three narrow but sufficient channels for the flame.

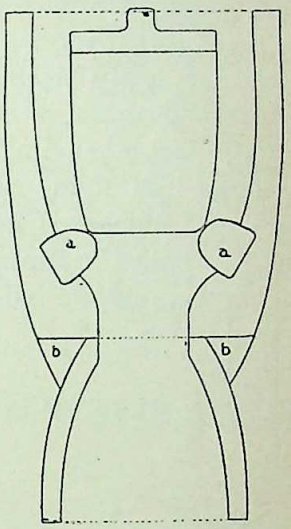


Fig. 2.—"Corset-shaped" graphite lining, composed of two graphite crucibles, base to base, showing supporting plugs (*a*), and small crucible in place. *b* is a ring of asbestos plaster around the joint between the two crucibles.

To minimize the effects of cracking, which may occur with a non-metallic lining, the lining is wrapped with asbestos cord, with or without a thin coat of asbestos plaster. If the graphite linings were made to order, better results would doubtless be had. We are now in correspondence with a well-known graphite firm, to this end.

This form of furnace lends itself readily to the addition of arrangements for preheating, the air or both the air and gas being heated in coils of pipe in a chimney above the combustion chamber, and led down in pipes through the powder just outside the lining, to the bottom. The preheating coils are thus readily accessible.

Of course the crucible may be supported in other ways than as described. If obtainable, a circular support of graphite, clay, or iron, with three prongs projecting inwards, or inward and upward, may be used with advantage, instead of the triangle. Further, either this support or the triangle arrangement might be so adapted as to be attached to the movable bottom fastened to the burner, thus admitting of the removal of the furnace from around the crucible without disturbing the latter, which is sometimes of advantage. Or by using a crucible molded with projecting lugs near its upper edge, fitting into corresponding lugs on the interior of the furnace, the entire bottom and sides of the crucible could be exposed to the flame, without the intervention of any supporting points.

This furnace, with both iron and graphite linings, has been used a

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number of times, and has shown its ability to melt copper and brass readily, and with more difficulty, cast iron.

It has been observed in the use of this furnace, that paper pasted on the outside of the outer container was charred only to a light brown, even when the furnace was maintained for several hours at the melting point of copper or even cast iron, during a part of which time a portion of the flame played about the outside of the flame-opening at the bottom; the powder lining in this case was an inch and a quarter thick. On the other hand, a furnace with solid clay walls one and one-quarter inches thick (Hoskins No. 2), when maintained at a similar temperature for an hour, completely blackened paper pasted on the outside.

For small work, a convenient size for the outside container is that of a 5-pound ether can, six inches in diameter by seven inches high, while the sheet-iron lining may be made two and one-half to three inches in diameter, and seven inches high. The same principles of construction may be applied to furnaces of practically any size and shape.

The drawings are self-explanatory.

WASHINGTON, D. C.

SULFITE METHOD FOR SEPARATING AND IDENTIFYING CALCIUM AND STRONTIUM.

By J. I. D. Hinds.

Received February 20, 1911.

The difficulty which beginners in qualitative analysis experience in the separation and identification of calcium and strontium has led me to seek a method which might be easier and more satisfactory than those now in use. By study of the table of aqueous solubilities we learn that strontium sulfite is sparingly soluble (0.033 gram to the liter), while calcium sulfite is quite soluble (1.2 gram to the liter), and that strontium sulfite is considerably less soluble than strontium sulfate (0.11 gram to the liter). As to barium and strontium sulfites, the difference in solubility is small and not sufficient for separation. All these solubilities are increased in acid solutions, but not to the same degree. In the presence of sufficient hydrochloric acid barium ion is precipitated by sulfite ion, while strontium ion is not; in dilute acetic acid solution barium and strontium ions are precipitated, while calcium ion is not.

In this investigation I used a freshly prepared concentrated (nearly saturated) solution of sodium sulfite. If the solution is kept long, the sulfate in it is increased by oxidation and the reactions are not typical. In finding the precipitation limits I used standard solutions of calcium and strontium chlorides.

In order to compare the efficiency of the commonly used calcium sulfate with that of sodium sulfite, which I propose as the precipitant, I

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diluted the strontium solution to various degrees of concentration with water containing a slight excess of acetic acid and a sufficient quantity of the reagent, in the one case calcium sulfate and in the other sodium sulfite, bringing the mixture to boiling and letting it stand for a few minutes. The following results were obtained:

Concentration of strontium solution.	Reagent.	
	Calcium sulfate.	Sodium sulfite.
0.00005 Normal	No precipitate	Faint cloud
0.0001 Normal	No precipitate	Precipitate
0.0005 Normal	No precipitate	Precipitate
0.001 Normal	No precipitate	Precipitate
0.004 Normal	Faint cloud	Precipitate
0.005 Normal	Precipitate	Precipitate

It is thus seen that the sulfite ion in the presence of a slight excess of acetic acid will give a precipitate in a ten-thousandth normal solution of strontium ion (0.004 gram to the liter), while calcium sulfate requires a concentration 0.005 normal (0.2 gram to the liter); that is, the sulfite is about fifty times as sensitive as the sulfate in grams of strontium ion to the liter. In solutions more strongly acid the difference is greater, though the sensitiveness is diminished.

The calcium and strontium solutions yielded with ammonium oxalate the following results:

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	No precipitate
0.007 Normal	Faint cloud	Faint cloud
0.001 Normal	Precipitate	Precipitate

The sensitiveness of the calcium and strontium ions to the oxalate ion thus appears to be about the same and the precipitation limit is not far from that of strontium sulfite. This relationship is but little changed in the presence of acetic acid, though the sensitiveness is diminished.

The precipitation limits for the sulfites of calcium and strontium were then determined under four conditions: (1) With the sulfite solution alkaline by hydrolysis, cold. (2) The same with the mixture boiled. (3) The sulfite solution made slightly acid with acetic acid and the mixture boiled. (4) The sulfite solution made more strongly acid and the mixture boiled.

1. The sulfite solution alkaline, cold, the mixture well shaken:

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	No precipitate
0.001 Normal	No precipitate	Faint cloud
0.0015 Normal	No precipitate	Precipitate
0.002 Normal	No precipitate	Precipitate
0.006 Normal	No precipitate	Precipitate
0.008 Normal	Faint cloud	Precipitate
0.01 Normal	Precipitate	Precipitate

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2. Sulfite solution alkaline and the mixture boiled:

Concentration.	Calcium	Strontium.
0.00005 Normal	No precipitate	Faint cloud
0.0001 Normal	No precipitate	Precipitate
0.0005 Normal	Faint cloud	Precipitate
0.001 Normal	Precipitate	Precipitate

We thus see that the alkaline sulfite makes a rather complete precipitation of both the calcium and the strontium.

3. The sulfite solution slightly acid with acetic acid, the mixture boiled:

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	Faint cloud
0.001 Normal	No precipitate	Precipitate
0.003 Normal	No precipitate	Precipitate
0.005 Normal	Precipitate	Precipitate

4. The sulfite solution strongly acid with acetic acid, the mixture boiled:

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	No precipitate
0.001 Normal	No precipitate	No precipitate
0.0015 Normal	No precipitate	Precipitate
0.01 Normal	No precipitate	Precipitate
0.1 Normal	No precipitate	Precipitate
1.0 Normal	No precipitate	Precipitate
1.2 Normal	Cloud	Precipitate
1.3 Normal	Precipitate	Precipitate

With acid of this strength the concentration of the filtrate is only 0.001 normal in strontium while it is 1.3 normal in calcium. If the solution is not higher than this in calcium, the separation of calcium and strontium is almost complete. If the solution is stronger, more acid may be added and still the separation will be good, since the strontium is practically all precipitated when the mixture is boiled, even in the presence of much acid. When the salts are mixed, some calcium remains in the precipitate, possibly because of oxidation to sulfate which seems to be less soluble in the acid than the sulfite.

The quantity of strontium which remains in the solution after the precipitation with the sulfite in the presence of acetic acid is just at the precipitation limit of strontium oxalate and the filtrate will give no precipitate with ammonium oxalate, or only a faint cloud. If it be diluted with an equal quantity of water, no precipitate falls. On the other hand, the calcium has largely remained in solution and will be precipitated by the oxalate ion. Calcium is thus sharply and easily separated from strontium. The strontium precipitate may contain some calcium from which it is not easily separated. The strontium will generally be satisfactorily identified by the flame reaction as described below.

Guided by the above facts, I have devised a modified method of analy-

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sis for the barium group which in repeated trials by myself and my students has been found to be eminently practical and easy.

1. Precipitate the elements of the group as carbonates, wash, and dissolve in the least quantity of warm, dilute acetic acid in the usual way.

2. Preliminary testing.

a. Add to 1 cc. of the solution in a test tube a few drops of hydrochloric acid, then 1 cc. of a freshly prepared concentrated solution of sodium sulfite. A precipitate is barium sulfite and proves the presence of barium.

b. Add to 1 cc. of the solution a few drops of dilute acetic acid, then 1 cc. of the sulfite solution. A precipitate is barium or strontium sulfite; in the absence of barium, it can only be strontium.

c. If barium and strontium are absent, add to 1 cc. of the solution 1 cc. of the sulfite solution. A precipitate is calcium sulfite, easily soluble in acetic acid.

3. Remove barium ion, if present, with dichromate ion and free the filtrate from dichromate ion by precipitation as carbonate and solution in dilute acetic acid in the usual way. The removal of the dichromate ion is generally not necessary, since the reactions are not seriously disguised by it.

4. To 5 cc. of the solution of 3 (or of 1, if barium is absent) add about 3 cc. of the sulfite solution, or enough for complete precipitation. A precipitate may be calcium or strontium sulfite. No precipitate does not indicate their absence. In either case, add about 1 cc. of dilute acetic acid, or just enough to dissolve or nearly dissolve the precipitate. Avoid much excess. If much strontium is present, it will not dissolve. Heat to boiling and set aside until the precipitate has mostly subsided. Pour the liquid on a filter leaving the bulk of the precipitate in the test tube. If the filtrate is cloudy, pass it through the filter again and again until it is perfectly clear.

The filtrate will contain most of the calcium and very little strontium.

The precipitate is strontium sulfite, but may contain some calcium sulfite.

5. Add to 5 cc. of the filtrate of 4 a little ammonium oxalate solution. A precipitate is calcium oxalate. If there is only a faint cloud, it may be due to strontium. In this case, dilute another portion of the filtrate with an equal volume of water and add the oxalate. The precipitate now must be calcium oxalate, since the strontium concentration has been reduced below the precipitation limit of strontium oxalate.

6. Cover the precipitate of 4 in the test tube with hydrochloric acid and heat to boiling. Test on platinum wire in the flame for strontium. If much calcium is present, there may be enough in the precipitate to mask the strontium flame. In this case, a very sharp distinction can be made

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as follows: Use two platinum wires, dipping one in a pure hydrochloric acid solution of a calcium salt and the other in the solution to be tested. Insert the middle of the wires in opposit sides of the Bunsen flame near its base and draw them slowly forward until the looped ends are in the flame. The sodium (and potassium if dichromate has been used) burns off first and leaves the more persistent calcium and strontium in the flame. A decided difference in the flame colors thus brought side by side is caused by even a trace of strontium.

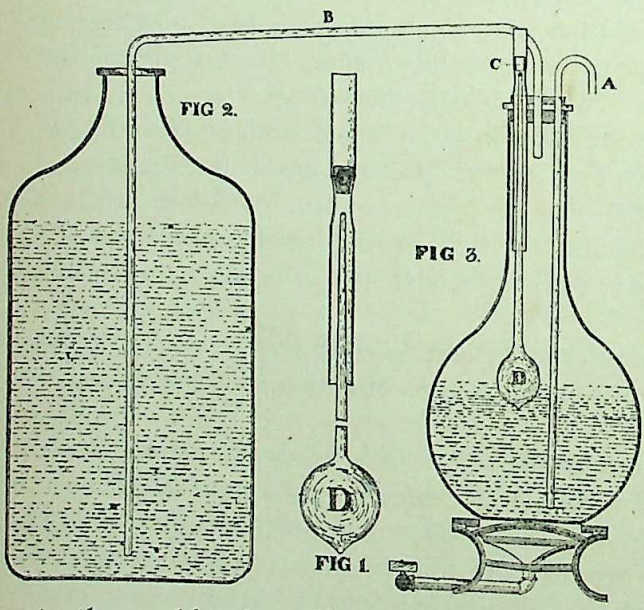
7. For futher confirmation of strontium add calcium sulfate solution to a portion of the solution of 3 and boil. A slowly forming precipitate indicates strontium.

The chief advantage of this method lies in the easy and unmistakable identification of calcium in the presence of strontium.

UNIVERSITY OF NASHVILLE,
NASHVILLE, TENN.

NOTES.

A Wash Bottle for Continuous Hot Water Supply.—It is often found very desirable, where a large amount of routine analytical work is done, to have a more convenient means of washing precipitates than that furnished by the common wash bottle. A wash bottle which has given very good satisfaction in this laboratory is described below in detail.



It consists of a heavy, 5-liter boiling flask (Fig. 3) connected with a large supply bottle (Fig. 2). The boiling flask has a tight-fitting three-holed rubber stopper as shown in the diagram. Through one hole passes a glass tube, *A*, which is connected by rubber tubing to the washing-jet. The tube *B* connects the supply bottle with the boiling flask. As the liquid in the boiling flask is lowered, there is a partial vacuum created which causes water from the supply bottle to pass through *B* into the boiling flask, thus maintaining the supply.

To allow the escape of steam from the boiling flask and to prevent

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the latter from filling to the stopper, due to the condensation caused by the cold water from the supply flask, a special valve (Fig. 1) is provided. This valve consists of a main tube which passes through the rubber stopper of the boiling flask. This tube, which may be ordinary 8 to 12 mm. tubing, is constructed as shown in the diagram in Fig. 1. Just above the constriction the tube is fitted with a ground glass plug. This plug is made the proper size by rotating in the upper part of the constriction a glass rod of proper size, the end of which has been covered with powdered emery. The ground end is then cut off, making the plug (*C*) as shown. The upper end of the tube is partly closed to prevent the escape of the plug. Into the lower portion of the tube is inserted a float, *D*, which is free to move up through the tube and lift the plug *C*.

The length of the float is regulated by the amount of water desired in the boiling flask, which should not be lower than as shown in the diagram.

When the water from the supply flask raises the height of the liquid in the boiling flask, the float *D* is pushed upward till it raises the plug, allowing an inrush of air which destroys the vacuum formed by the condensation.

In order to obviate the risk of bursting the flask by the vacuum produced through condensation of the steam, a safety mercury valve is advisable. This is easily made by bending a glass tube so that one end may be fitted through the stopper of the boiling flask and the other end dipping into a small vessel of mercury. About six inches from the lower end of the tube should be a bulb large enough to hold twice the amount of mercury used.

The bulb of the float should be as large as the neck of the flask will admit. The whole apparatus can be constructed by any one of ordinary skill.

G. E. Boltz.

Ohio Agricultural Experiment Station, Wooster, O.

Some Experiments on the Formation of Ammonia from Its Elements.—The recent papers by Lipski[1] and by Haber,[2] on the direct synthesis of ammonia from its elements, have brought to mind some few random observations made by the writer with a similar aim in mind, during the last two years. The experiments were almost entirely qualitative, and were discontinued partly for the reason that they did not seem to offer very much encouragement for further study. The experiments may be divided into three classes: (*a*) purely catalytic, (*b*) semi-catalytic, and (*c*) electrical.

(*a*) The catalytic experiments consisted in the passage of the mix-

[1] "Ueber Synthese des Ammoniaks aus den Elementen," Dissert., Herzogl. Tech. Hochschule Carolo-Wilhelm. Braunschweig, Halle, 1909.

[2] *Chem. Ztg.*, 34, 345.

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ture $3H_2 + N_2$ over various reagents which seemed to offer some possibility of effecting the union of the nitrogen and hydrogen. The gases were passed over at atmospheric pressure, and at temperatures of 20°, 100°, 300° and red heat, and the catalytic agents tried were platinized asbestos, palladium-asbestos, reduced iron, and finely powdered commercial 85 per cent. ferromanganese. Traces of ammonia were found in the water through which the outflowing gases were passed, from each of these agents, the ferromanganese showing decidedly the greatest activity. The ammonia was tested for by means of Nessler's reagent, and in most cases showed amounts comparable to the higher standards used in sanitary water analysis—say a maximum of 0.00006 gram of NH_3—after the passage of volumes of gases varying from one liter to ten liters.

(*b*) The semi-catalytic experiments consisted in passing mixtures of steam and nitrogen at 100° and atmospheric pressure over substances which would decompose the water vapor, and taking up the oxygen, theoretically leave the hydrogen in the nascent condition. Iron filings, zinc dust, and sodium amalgam (2 per cent.) were tried and as in the (*a*) experiments, traces of ammonia were found in the water through which the gases were drawn, but again not in sufficient quantity to warrant further development with the materials used.

Steam passed over calcium cyanamide yielded ammonia in abundance, as is well known, but this is a two-stage process, and not strictly in line with the other experiments.

(*c*) The third series of experiments was conducted at the suggestion of Dr. Norman Roberts, and with his aid and direction. For the most part they consisted in the passage of an electric spark between platinum electrodes in a mixture of hydrogen, nitrogen and hydrochloric acid gases, under both atmospheric and increased pressure. Fumes were frequently seen in the reaction vessel following the sparking, and these appeared to settle on the walls of the container. Yet when the vessel was washed out with ammonia-free water, and the wash water tested with Nessler's reagent, the amount of ammonia present was too small to warrant these fumes being considered as ammonium chloride.

Apparently the synthesis of ammonia *can* be effected in any of these ways, and it is possible that if the action were continued for a sufficient length of time upon a limited quantity of mixed gases, under conditions such that the ammonia would be absorbed as soon as formed, the yield of ammonia might be approximately quantitative, but the time element is of such magnitude as to render any of these processes of no merit practically.

Of course, one difficulty which is inevitably present in any work of this kind is the ease with which ammonia dissociates at high temperatures, and it is of interest to note that in those experiments which have yielded

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the best results in the papers above cited, pressures ranging from 11 to 200 atmospheres have been employed.

F. ALEX. MCDERMOTT.
WASHINGTON, D. C.

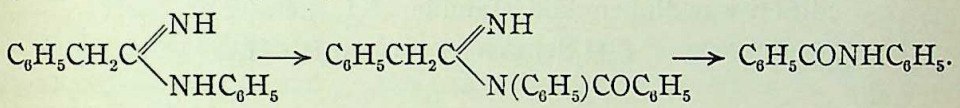
[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

BENZOYLPHENYLACETAMIDE.

BY TREAT B. JOHNSON AND LEWIS H. CHERNOFF.

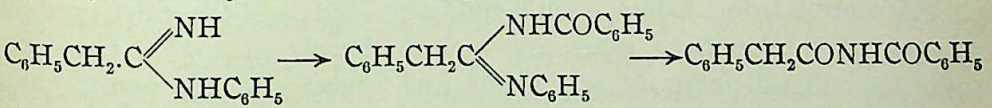
Received January 25, 1911.

In a paper entitled "The Molecular Rearrangement of Unsymmetrical Acylamidines into Isomeric Symmetrical Derivatives", Wheeler, Johnson and McFarland[1] described the behavior of benzoylchloride towards phenylacetophenylamidine, I. They observed that they reacted in anhydrous ether, at ordinary temperature, giving an unsymmetrical benzoyl derivative, II, melting at 110–111°. The structure of this compound was established by the fact that it smoothly underwent hydrolysis with hydrochloric acid, giving benzanilide, III.



I. II. III.

In one experiment, however, in which chloroform was used as the solvent instead of ether, the reaction was less smooth and the primary products of the reaction—acylamidines—were not isolated. Under these conditions a mixture of benzanilide and a compound, to which they assigned the structure of benzoylphenylacetamide, V, was obtained. The latter contained 6.1 per cent. nitrogen and it was soluble in cold alkali and melted at 129–130°. An amide of this structure would result by the hydrolysis of a symmetrical benzoyl derivative, IV.



IV. V.

Our attention has recently been called, by the revisers of Beilstein's Handbuch, to the fact that this diacidamide, V, had previously been described by Colby and Dodge,[2] who assigned to it the much higher melting point of 171°. They obtained it by heating benzonitrile, VI, and phenylacetonitrile, VIII, with phenylacetic, VII, and benzoic acids, IX, respectively at a high temperature. They state that the same compound, melting at 171°, was obtained in both reactions, and that it underwent hydrolysis with alkali, giving phenylacetic and benzoic acids. Their syntheses are expressed by the following equations:

[1] THIS JOURNAL, 25, 787.
[2] *Am. Chem. J.*, 13, 6.

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$$\begin{matrix} C_6H_5CN \\ \text{VI.} \end{matrix} + \begin{matrix} C_6H_5CH_2COOH \\ \text{VII.} \end{matrix} \rightarrow \begin{matrix} C_6H_5CH_2CONHCOC_6H_5 \\ \text{V.} \end{matrix}$$

$$\begin{matrix} C_6H_5CH_2CN \\ \text{VIII.} \end{matrix} + \begin{matrix} C_6H_5COOH \\ \text{IX.} \end{matrix} \rightarrow \begin{matrix} C_6H_5CH_2CONHCOC_6H_5 \\ \text{V.} \end{matrix}$$

The writers have now reexamined the action of benzoyl chloride on phenylacetophenylamidine and find that the original conclusions were correct. Working under the same conditions, we obtained again the same diacidamide, melting at 129–130°, and it underwent hydrolysis giving benzoic and phenylacetic acids. Furthermore, we have prepared this same diacidamide, V, by a new method. We find that it is formed almost quantitatively by the action of benzoylisocyanate,[1] X, on phenylacetic acid at ordinary temperature.

$$\begin{matrix} C_6H_5CO.NCO \\ \text{X.} \end{matrix} + C_6H_5CH_2COOH = \begin{matrix} C_6H_5CH_2CONHCOC_6H_5 \\ \text{V.} \end{matrix} + CO_2.$$

An attempt to prepare the amide by the action of benzoylisothiocyanate on phenylacetic acid was unsuccessful. The only product isolated in a pure condition was diphenyldiacetamide, XI, melting at 192°.

$$C_6H_5CO.NCS + C_6H_5CH_2COOH \longrightarrow \begin{matrix} (C_6H_5CH_2CO)_2NH. \\ \text{XI.} \end{matrix}$$

These interesting results naturally led us to repeat the experiments of Colby and Dodge.[2] Following carefully their directions, we heated benzonitrile with phenylacetic acid and also phenylacetonitrile with benzoic acid, but obtained in neither case a diacidamide, melting at 171°. We obtained a crystallin substance which melted, after one crystallization from alcohol, at about 170°, but it was at once apparent, by examination under the microscope, that this was not a definit compound but a mixture. It was identified as a mixture of dibenzamide and diphenyldiacetamide, which were easily separated from each other by fractional crystallization from alcohol. Diphenyldiacetamide was the chief product of the reaction in both cases and melted sharply at 192°. These results explain satisfactorily why Colby and Dodge obtained benzoic and phenylacetic acids by hydrolysis of their supposed amide with alkali. A mixture of the two above amides would give the same acids on hydrolysis as pure benzoylphenylacetamide. Therefore, *benzoylphenylacetamide melts at 129–130° and not at 171°.*

Experimental Part.

Action of Benzoylisocyanate on Phenylacetic Acid. Formation of Benzoylphenylacetamide, $C_6H_5CONHCOCH_2C_6H_5$.—The benzoylisocyanate used for this preparation was prepared according to Billeter's directions,[2] by the action of benzoylchloride on silver cyanate.

Five grams of the freshly distilled isocyanate were poured upon 5 grams

[1] Billeter, *Ber.*, 36, 3218.

[2] *Loc. cit.*

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of dry phenylacetic acid, in a dry flask. They reacted immediately with violence and with evolution of carbon dioxide giving a clear liquid, which solidified in a few minutes. After heating on the steam bath for about 1 hour, to complete the reaction, the reaction product was treated with alcohol, when we obtained two substances differing decidedly in solubility in this solvent.

The chief amount was very soluble in hot alcohol and separated, on cooling, in colorless needles. After recrystallization from absolute alcohol, it melted sharply at 129–130° to a clear oil, and was identified as benzoylphenylacetamide. The compound was absolutely identical with the diacidamide obtained by the action of benzoylchloride on phenylacetophenylamidine.[1] A mixture of the two melted at the same temperature. A mixture of the diacidamide and benzamide melted at 105–115°. The compound was decomposed by alkali giving a mixture of benzoic and phenylacetic acids. Analysis (Kjeldahl):

Calculated for $C_{15}H_{13}O_2N$:	N, 5.8 ;	C_7H_7ON, 11.5.
Found:	N, 6.00;	6.1

The product difficultly soluble in alcohol was identified as dibenzoylurea and melted at 208–211°. A nitrogen determination gave (Kjeldahl):

Calculated for $C_{15}H_{12}O_3N_2$: N, 10.4; Found, 10.0 per cent.

Action of Benzoylisothiocyanate on Phenylacetic Acid. Formation of Diphenyldiacetamide, $(C_6H_5CH_2CO)_2NH$.—This isothiocyanate reacts less energetically with phenylacetic acid than the corresponding benzoylisocyanate. Five grams of phenylacetic acid were dissolved in 5 grams of benzoylisothiocyanate and the solution heated in an oil bath at 104–110°. Carbonoxysulfide was slowly evolved and after heating about 17 hours the oil finally solidified. This product behaved in every respect like a mixture. After two crystallizations from 95 per cent. alcohol it separated in uniform crystals and melted at 170–175° but the melt was turbid in appearance and did not become transparent until heated to 185°. After several recrystallizations of this apparently homogeneous substance, a constant melting point of 191–192° was obtained and the compound identified as diphenyldiacetamide. A mixture of the compound and some pure diphenyldiacetamide melted at the same temperature. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.53. Found, 5.7.

Action of Benzonitrile on Phenylacetic Acid.—Ten grams of the nitrile, 13.6 grams of phenylacetic acid and 3 drops of acetic anhydride were heated in a sealed tube for 5 hours at 200°, then 5.5 hours at 240° and finally for 2 hours at 260°. When the tube was opened, we obtained a colorless, crystallin substance suspended in some oil having the charac-

[1] Wheeler, Johnson and McFarland, *Loc. cit.*

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teristic odor of benzonitrile. The solid was purified by crystallization from 95 per cent. alcohol and melted, after the third crystallization, constant at 192°. It was identified as diphenyldiacetamide. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.53; Found, 5.59.

Action of Phenylacetonitrile on Benzoic Acid.—Ten grams of the nitrile and 10.4 grams of benzoic acid were heated for 5 hours at 240° and finally for 2 hours at 260°. On opening the tube we obtained a crystallin substance and an oil having the odor of benzonitrile. The solid was triturated with a little cold 95 per cent. alcohol to remove the oil, and melted without further purification at about 166–172° to a turbid liquid. It behaved in every way like a mixture, and after two recrystallizations from alcohol the melting point was raised to 192° indicating the presence of diphenyldiacetamide. A mixture of the compound and some diphenyldiacetamide from the previous experiment melted at exactly the same temperature. The alcoholic filtrates, after crystallization of the diacidamide, were combined and concentrated. On cooling, colorless prisms finally separated, which melted, not sharply, at 145–147°. Not enough of this material was obtained sufficiently pure for analyses, but its melting point, and the fact that it was decomposed by alkali giving only benzoic acid, indicated that it was dibenzamide.

Action of Benzoylisocyanate on β-Phenylpropionic Acid. Formation of β-Phenylpropionylbenzamide,[1] $C_6H_5CONH.CO.CH_2CH_2C_6H_5$.—Benzoylisocyanate and the above acid reacted almost immediately, on mixing, with evolution of heat and carbon dioxide. After heating at 100° for a few minutes the reaction was complete and the diacidamide was obtained in a crystallin condition. The yield was practically quantitative. It crystallized from alcohol and melted at 104–105° to a clear oil. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.35; Found, 5.14.

NEW HAVEN, CONN.,
January 21, 1911.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

2,3-DIMETHYLHEXANE.

BY LATHAM CLARKE.

Received February 8, 1911.

This paper contains first an account of the preparation and properties of 2,3-dimethylhexane, $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, the study of which has been taken up in continuation of a research on the octanes begun some time ago in the laboratory;[2] and second, a comparison of eight octanes, *viz.*, normal octane, the three methylheptanes, and the

[1] Colby and Dodge, *Loc. cit.*

[2] Preliminary Notice, *Ber.*, 40, 352.

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four dimethylhexanes, which last series, the synthesis of 2,3-dimethylhexane now completes.

The graphical formulas of the above-mentioned octanes are as follows:

1. $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, Normal.[1]
2. $CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH_3$, 2–Methylheptane.[2]
3. $CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$, 3–Methylheptane.[3]
4. $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$, 4–Methylheptane.[4]
5. $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3–Dimethylhexane.[5]
6. $CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH_3$, 2,4–Dimethylhexane.
7. $CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$, 2,5–Dimethylhexane.[6]
8. $CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$, 3,4–Dimethylhexane.[7]

A table of the boiling points, specific gravities and indices of refraction of these hydrocarbons follows:

		Boiling point.	Specific gravity. 15°/15°.	Index of refraction N_D (25°).
1	Normal octane.....	124.7° at 760 mm	0.7068	1.3963
2	2-Methylheptane	116.0° at 761 mm	0.7035	1.3944
3	3-Methylheptane	117.6° at 760 mm	0.7167	1.4022
4	4-Methylheptane	118.0° at 760 mm	0.7217	1.3978
5	2-3-Dimethylhexane.....	113.9° at 758 mm	0.7246	1.4075
6	2,4–Dimethylhexane.....	110.0° at 763 mm	0.7083	1.3986
7	2,5–Dimethylhexane.....	108.25° at 760 mm	0.6991	1.3930
8	3,4–Dimethylhexane.....	116.5° at 759 mm	0.7279	1.4038

Normal Octane.—The boiling point and other constants given above were determined in this laboratory.[8]

2-Methylheptane.—Data obtained from the hydrocarbon prepared by two methods.[9]

3-Methylheptane.—Data obtained from the hydrocarbon made in this laboratory.[10] Mlle. Welt[11] gives the boiling point 110° to 120° but her compound was evidently not very pure.

4-Methylheptane.—Data obtained from a sample made in this laboratory.[12]

[1] T. Riche, *Ann.*, 117, 265; Schorlemmer, *Ibid.*, 161, 280; 152, 152; 147, 227; Zincke, *Ibid.*, 152, 15; Paterno and Peratoner, *Ber.*, 22, 467.

[2] Clarke, THIS JOURNAL, 31, 107 (1909).

[3] Welt, *Ann. chim. phys.*, [7] 6, 121; Clarke, THIS JOURNAL, 31, 558.

[4] Clarke, *Ber.*, 40, 352; *Amer. Chem. J.*, 39, 87.

[5] Clarke, THIS JOURNAL, 30, 1144.

[6] Wurtz, *Ann.*, 96, 365; Schorlemmer, *Ibid.*, 114, 188; Kolbe, *Ibid.*, 69, 261; Young, *J. Chem. Soc.*, 77, 1136; Clarke, THIS JOURNAL, 31, 585.

[7] Norris and Green, *Am. Chem. J.*, 26, 313. This octane also has been made in this laboratory, but the work is as yet unpublished.

[8] Other authors state the following boiling points: Thorpe, *Soc. Trans.*, 37, 77, 125.46°; Young, *Soc.*, 77, 145, 125.8° at 760 mm. The specific gravity is given by Thorpe as 0.71883 at 0°/4°, and by Young as 0.71850, 0.71817 and 0.71848 at 0°/4°.

[9] Clarke, THIS JOURNAL, 31, 114, 116.

[10] Clarke, *Ibid*, 31, 559.

[11] *Ann. chim. phys.*, [7] 6, 121.

[12] ***Am. Chem. J.*, 39, 96.**

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2,3-Dimethylhexane.—These data are the average of the results obtained when the hydrocarbon was made by two methods as explained later in this paper.

2,4-Dimethylhexane.—Data obtained from the octane made by two methods.[1] These gave the following results:

	Boiling point.	Specific gravity, 15/15	Index of refraction, N_D 25°.
First Method.....	109.8°–110° at 762 mm.	0.7083	1.3986
Second Method.....	110.0° at 763 mm.	0.7083	1.3986

2,5-Dimethylhexane.—The above data are the average of the results obtained from specimens of the hydrocarbon prepared by two methods.[2]

		Specific gravity, 15/15.	Index of refraction, N_D 25°.
First Method.....	108. – 108.3° at 760 mm.	0.6989	1.3926
Second Method.....	108.3 – 108.5° at 760 mm.	0.6993	1.3935
Average.....	108.25°	0.6991	1.3930

Other observers have published the following data which have been collected by Young and Fortey.[3]

	Boiling point at t°.	Corrected to 760 mm.
Kolbe, *Ann.*, 69, 259 (1849).....		108°.
Kopp, *Ann.*, 95, 335 (1855).....	108.5° at 747.5 mm.	109.1°
Thorpe, *J. Chem. Soc.*, 37, 219 (1880)...	108.2°–108.7° at 748.2 mm.	108.53°
Schiff, *Ann.*, 220, 88 (1883).....	107.8°–107.9° at 751.4 mm.	108.25°
Williams, *Ann.*, 35, 125 (1879).....	108.2° at 745. mm.	108.9°
Pawlewski, *Ber.*, 16, 2634 (1883)		107.5°
Young and Fortey, *Loc. cit.*.....		109.2°

	Specific gravity at t°.	Calculated at 0°/4°.
Kolbe, *Jahresb.*, 1, 559 (1848).....	0.6940 at 18°.	0.7091
Wurtz, *Jahresb.*, 8, 576 (1855).....		0.7057
Kopp, *Loc. cit.*.....		0.7135
Williams, *Loc. cit.*.....		0.7091 0.7085
Schorlemmer, *Jahresb.*, 20, 567 (1867).....	0.698 at 16.5°	0.7119
Thorpe, *Loc. cit.*.....		0.7111
Schiff, *Loc. cit.*.....	0.7001 at 12.1°/4°	0.7103
Young and Fortey, *Loc. cit.*.....	0.69996 at 11.9°/4°	0.71021

3,4-Dimethylhexane. — Data observed in this laboratory on a sample prepared by the action of sodium on 2-iodobutane following the method described by Norris and Green.[4]

[1] Clarke, THIS JOURNAL, 30, 1148, 1151.
[2] Clarke, *Ibid.*, 31, 588, 589.
[3] *J. Chem. Soc.*, 77, 1137.
[4] *Am. Chem. J.*, 26, 318.

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Their data were as follows: Boiling point, 116° to 116.2° at 750 mm. pressure. Specific gravity, 0°/4°, 0.7332, at 25°/4, 0.7165.

A study of the table of physical properties now reveals some interesting relationships.

The octanes here seem to fall into three classes: First, normal octane stands by itself for its boiling point is nearly seven degrees higher than the next lower, whereas its specific gravity is lower than most of the others, in fact, but two of the eight given are higher than it, and it stands in the same position in regard to relative index of refraction. Second, the methylheptanes form a group of three. Between the boiling point of the lowest and the boiling point of the highest boiling there is a difference of but two degrees. 2-Methylheptane boils the lowest; on moving the methyl group to the 3-position, an increase of 1.6° is observed, and on moving the methyl to the 4-position a further increase of 0.4° is brought about. As the boiling point rises, the specific gravity increases but in much greater proportion. We should expect the indices of refraction to follow the specific gravities, and as the latter increases, so should the former. But this does not appear to be so, 4-methylheptane has the greatest specific gravity of the three, but the index of refraction is less than that of 3-methylheptane. Third, the dimethylhexanes form a group of four. The physical constants exhibit a wider range than do those of the methylheptanes. The lowest boiling member of this series is 2,5-dimethylhexane, *viz.*, 108.25°; this has also the lowest specific gravity and lowest index of refraction. Next above 2,5-dimethylhexane in boiling point comes 2,4-dimethylhexane, above this 2,3-dimethylhexane, and highest of all comes 3,4-dimethylhexane. The specific gravities rise with increasing boiling point and the index of refraction follows this order too, with the exception of the 3,4-dimethylhexane, which has an index lower than that shown by the compound when the methyl groups are in the 2,3-position.

These three classes, into which the octanes enumerated thus divide themselves, have the following essential difference in structure. The normal compound contains two methyl groups, the methylheptanes contain three, and the dimethylhexanes four. Increasing the number of methyl groups increases the volatility of the compound and we can now establish a set of comparative data in this subject.

The boiling point of normal octane is 124.7° while that of 2-methylheptane is 116.0°, which shows a lowering of 8.7° in going from a straight chain containing eight carbon atoms with two methyl groups to a chain containing seven members and three methyl groups. This is a greater difference than exists between normal and iso-hexane, and normal and iso-heptane, as shown by the following table:

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	Boiling point at 760 mm.	Difference.
Hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$.....	68.8[1]	
Isohexane, $CH_3CH(CH_3)CH_2CH_2CH_3$.....	62.0 [2]	6.8°
Heptane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$.....	98.2 – 98.5 Ave. 98.35° [3]	
Isoheptane, $CH_3CH(CH_3)CH_2CH_2CH_2CH_3$...	Ave. 90.3	8.0°

The fact is here brought out that with increasing molecular weight and increasing length of carbon chain, the lowering effect of the "iso group" becomes greater and greater.

In considering the dimethyl hexanes, it can now be shown that the boiling point of the 2,5-dimethylhexane is about as much lower than the boiling point of 2-methylheptane as isoheptane is lower than normal heptane.

2-Methylheptane (or iso-octane) has the boiling point 116°. We have now a straight chain *seven* carbon atoms in length, and if we now replace our normal groups at the opposit end of the chain by an iso group, we observe the lowering is the same as that which takes place in going from normal heptane to isoheptane, which is 8°, *viz.*: 116.0 — 8.0° = 108.0°. The actual is 108.25°, which is probably within the limits of experimental error.

	Boiling point.	Difference.
$CH_2CH_2CH_2CH_2CH_2CH_2CH_2$.....	98.35°	
$CH_3CH(CH_3)CH_2CH_2CH_2CH_3$.....	90.3°	8.0°
$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$.....	116.0°	
$CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$.....	108.25°	7.75°

Taking now the case of 2,4-dimethylhexane or calling it 3,5-dimethylhexane for the sake of clearness, we should expect from the above relations that the boiling point would be as much lower than that of 3-methylheptane, as isoheptane is lower than normal heptane, *viz.*, 8.0° lower.

	Boiling point.	Difference.
$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$, 3-methylheptane.....	117.6°	
$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_3$, 2,4-dimethylhexane or 3,5-dimethylhexane...	110° at 763	7.6°

The boiling point of 2,4-dimethylhexane corrected to 760 mm. would be slightly less than 109.9°, making the difference here 7.7°, so that this also is a very fair agreement.

By the same method of calculation, the boiling point of 2,3-dimethylhexane should be the same as that of 3,5-dimethylhexane, *viz.*, 117.6° — 8.0° = 109.6°. But instead of being 109.6°, it is 113.9°, which is 4.3° higher.

[1] Average of Young, 68.95°, *Soc.*, 73, 906; and Friedel and Gorgen, 68.60°, *Compt. rend.*, 127, 592.

[2] Observed in this Laboratory in sample made by method described in the *Am. Chem. J.*, 35, 513.

[3] Young, *Soc.*, 73, 906.

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		Boiling point.
$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$,	3-methylheptane	117.6°
$CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$,	2,3-dimethylhexane	113.9°

The methyl groups no longer act independently of each other as they apparently have in the two previous cases, but here they are attached to adjacent carbon atoms whereas in the other cases the carbon atoms to which they were joined were separated by one or more —CH_2— groups.

In 3,4-dimethylhexane, we have a configuration similar to that of 2,3-dimethylhexane, and here again the observed boiling point is higher than that which may be calculated as follows. The boiling point of 3-methylhexane is 7.3° lower than that of the normal heptane:

	Boiling point.
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$.....	98.35°
$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$.....	91.°[1]

Starting now with 4-methylheptane and replacing the —$CH_2CH_2CH_2CH_3$ group by —$CH(CH_3)CH_2CH_2$, we might expect to get a lowering of 7.3°; since this would be parallel to the foregoing calculations, this would give for 3,4-dimethylhexane, the boiling point 110.7°, but the actual is 116.5°, which is 5.8° higher.

	Boiling point.
$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$.....	118°
$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$.....	116.5°

These results seem to show that the methyl group tends to produce volatility, for the methylheptanes containing three methyl groups boil several degrees lower than the normal octane, which contains but two. The position of the methyl group makes only a slight difference in the boiling points, since those of the three methyl heptanes are within two degrees of one another. The density of the compounds rises as the methyl group is moved successively from the 2-, to the 3-, or to the 4-position. This may be due to the repellent action of CH_3 groups towards each other, making the compound containing the methyl in the 2-position least compact, producing a liquid of less density than for example, the 4-methylheptane, where the methyl groups are farther removed, and which is a compound of relatively high specific gravity.

In the case of 2,5-dimethylhexane, we have four methyl groups, and each pair of CH_3 groups acts independently of the other, giving a very volatil compound, and as has already been explained, the introduction of the second "iso group" into the iso-octane or methylheptane has produced the lowering of 8° which was characteristic of the heptanes

[1] Just, *Ann.*, 220, 154. This hydrocarbon has also been made by Mlle. Welt, *A. Chem.*, [7] 6, 121, who observed the boiling point, 80–88°, but her compound was evidently not very pure. The physical properties of this hydrocarbon will be determined as soon as possible in this laboratory.

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themselves. The compound is the least dense of the series and thus bears out the theory that methyl groups in the "iso" position have a repellent action on one another and produce a compound of relatively low specific gravity and boiling point.

With 2,4-dimethylhexane, the independence of action of the "iso" methyl group and that present on the No. 4 carbon atom is shown and the lowering of boiling point produced by substituting the straight chain in the 4-methylheptane by the "iso" group is that observed in the case of the two corresponding heptanes.

2,3-dimethylhexane has a boiling point higher by practically 4° than 2,4-dimethylhexane, while the two should boil at the same temperature, if the methyl groups were independent of each other. In this case the repellent action of the methyl groups is much more than overbalanced by the spatial configuration which is such that a compact molecule results, and to this may be ascribed the higher boiling point and greater density as compared to the 2,4-dimethyl compound. The same explanation applies to the observation that 3,4-dimethylhexane boils so high, —116.5°, and has the greatest density of any octane as yet obtained, its specific gravity being 0.7270 at 15°, compared to water at 15°.

Special Theoretical.

For the synthesis of 2,3-dimethylhexane two methods were employed: The first method consisted of the following steps: Ethyldimethylacetoacetate was prepared from methyl iodide and ethyl sodium acetoacetate, and by saponifying this dimethylacetone, or 2-methyl-3-butanone was obtained. From pure normal propyl alcohol, the corresponding carbinol bromine was made and from this in turn the organo-magnesium derivative. The action of this normal propylmagnesium bromide on 2-methyl-3-butanone produced the carbinol, 2,3-dimethyl-3-hexanol, which was converted into 2,3-dimethyl-3-iodohexane, and reduced, thereby yielding 2,3-dimethylhexane.

SUMMARY.

$CH_3COCH_2CO_2C_2H_5$, Ethylacetoacetate⟶
$CH_3COC(CH_3)_2CO_2C_2H_5$, Ethyldimethylacetoacetate⟶
$CH_3COCH(CH_3)_2$, 2-Methyl 3-butanone + $CH_3CH_2CH_2Mg\ Br$⟶
$CH_3CH_2CH_2—C(CH_3)\ (OH)CH(CH_3)CH_3$, 2,3-Dimethyl-3-hexanol⟶
$CH_3CH_2CH_2C(I)(CH_3)CH(CH_3)CH_3$, 2,3-Dimethyl-3-iodohexane.
$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_3$, 2,3-Dimethylhexane.

In synthesizing 2,3-dimethylhexane by the second method, the initial compound was ethylacetoacetate, from which ethyl methyl normal propylacetoacetate was prepared, and then saponified, forming 3-methyl-2-hexanone. This was treated with methyl-magnesium iodide, whereby 2,3-dimethyl-2-hexanol was produced, which was converted into the corresponding iodohexane and reduced, yielding 2,3-dimethylhexane.

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SUMMARY

$CH_3COCH_2CO_2C_2H_5$, Ethylacetoacetate⟶
$CH_3COCH(CH_3)—CO_2C_2H_5$, Ethyl methyl normal propylacetate⟶
$CH_2CH_2CH_3$
$CH_3COCH(CH_3)CH_2CH_2CH_3$, 3-Methyl-2-hexanone⟶
$CH_3CH(OH)(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-Dimethyl-2-hexanol⟶
$CH_3—C(I)(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-Dimethyl-2-iodohexane⟶
$CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-Dimethyl-hexane.

Both these methods are quite satisfactory but the second is to be preferred, as in the different steps better yields are obtained.

The hydrocarbons made by both methods were apparently identical. The physical constants were as follows:

	Boiling point.	Specific gravity, 15/15.	Index of refraction, N_D 25°.
Octane by Method No. 1....	113.8–114 at 760 mm.	0.7241	..
Octane by Method No. 2....	113.8–114 at 760 mm.	0.7252	1.4075
Average....	113.9° at 760 mm.	0.7246	1.4075

The difference in the above specific gravities is undoubtedly due to an experimental error. The amount of the hydrocarbon made by method No. 1 was barely enough to properly fill the pycnometer, and to this fact the differences in the results is undoubtedly due.

Experimental Part.

First Method.—In the preparation of ethyl dimethylacetoacetate from ethyl sodium acetoacetate and methyl iodide, many difficulties were encountered and good yields could not be obtained. It was found that the most satisfactory procedure was to make and use the ethyl mono-sodium acetoacetate in benzene solution and to allow this solution to stand with excess of methyl iodide for a week or more at room temperature, then to distil off the unchanged methyl iodide, extract the sodium iodide from theethylmethylaceto acetate by shaking out with water, dry the ethylmethylacetoacetate with solid potassium carbonate, and treat with a second molecule of sodium and methyl iodide in the manner just described, again allowing the mixture to stand for a week. In this way fairly good yields could be obtained.

It is best to illustrate this procedure by an experiment. 130 grams of ethylacetoacetate were mixed with 300 grams of dry benzene and to the solution 23 grams of sodium were added, a small piece at a time, with heating on the steam bath. When all the sodium had been dissolved, the solution was cooled and 175 grams of methyl iodide were added and the mixture allowed to stand for a week, best in a warm place. Any unchanged methyl iodide was then distilled off and the residue treated with enough water to remove the sodium iodide, after which the ethylmethylacetoacetate was dried with a small amount of potassium carbon-

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ate. To the dried benzene solution, 23 grams of sodium were introduced as before, and after the addition of 175 grams of methyl iodide again allowed to stand for a week. The ethyldimethylacetoacetate was then obtained by the same procedure of distilling off the excess of methyl iodide, treating with water to remove sodium iodide and drying with potassium carbonate, after which the benzene was distilled off on an oil bath. The yield of ethyl dimethylacetoacetate in this crude state was from 60 to 70 per cent. of the theoretical. It was not purified especially but was distilled once and then converted into the ketone $CH_3COCH(CH_3)$ by saponification.

The saponification of ethyl dimethylacetoacetate to 2-methyl 3-butanone was easily accomplished by boiling with 4 molecules of caustic potash in 10 per cent. aqueous solution for six hours, distilling with steam, separating and drying the upper layer of the distillate with calcium chloride, and fractionating with a long Hempel column. The ketone thus obtained boiled at 95–95.3° at 760 millimeters pressure.

2,3-Dimethyl-3-hexanol, $CH_3CH_2CH_2C(CH_3)(OH)CH(CH_3)CH_3$.—This compound was made in the manner of the following experiment: 4 grams of magnesium were dissolved in a mixture of 21 grams of normal propyl bromide and 20 grams of anhydrous ether, and to the cold solution 15 grams of 2-methyl-3-butanone, diluted with an equal volume of ether, were slowly added. After half an hour's standing, the carbinol was freed by the usual procedure of adding water and hydrochloric acid, drying the ether layer with potassium carbonate, and fractionating. Thus, 10 grams of carbinol were obtained, boiling at 158°–158.2°, at 758 millimeters pressure, after three distillations. From the method of formation it was known to be 2,3-dimethyl-3-hexanol, with the following constitution: $CH_3CH(CH_3)C(CH_3)(OH)CH_2CH_2CH_3$. The reaction was accompanied by the formation of two high-boiling liquids neither of which could be fractionated. The analysis was satisfactory.[1]

Properties: Liquid boiling at 158°–158.2° at 758 millimeters pressure and with a strong odor something like eucalyptus oil. It is miscible with the common organic solvents but immiscible with water.

Preparation and Reduction of 2-3-Dimethyl-3-iodohexane, $CH_3CH(CH_3)C(I)(CH_3)CH_2CH_2CH_3$.—Ten grams of 2,3-dimethyl-3-hexanol were mixed with 1.5 grams of red phosphorus and treated with 10 grams of iodine; the reaction flask at first was kept cold by a cold water bath but at the end of an hour was warmed to 60° and allowed to remain at that temperature for three hours. The carbinol iodide was purified, not by distillation, but by shaking out twice with cold water and filtering through glass wool to remove unchanged phosphorus. It

[1] During my absence of a year in Europe, the analytical note-book containing this and other numerical data was mislaid, and the figures are, therefore, not accessible.

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was then reduced by zinc and hydrochloric acid, and finally by scrap magnesium and hydrochloric acid to remove final traces of halogen. The resulting octane was distilled with steam from the reduction mixture, treated with concentrated sulphuric acid, shaken with dilute potassium permanganate solution until no more discoloration took place, boiled over sodium with a return condenser, and carefully fractionated. About 4 grams of octane were obtained in this way, practically all of which boiled at 113.8° to 114° at 758 millimeters. The liquid was halogen-free and contained no unsaturated hydrocarbon. The analysis was satisfactory.

Properties: Colorless, very mobil liquid, boiling at 113.8° to 114° at 758 millimeters pressure, and with a rather strong odor. It has at 15° the specific gravity 0.7241 compared to water at 15°.

Second Method.—Ethyl methyl normal propyl acetoacetate was made from ethyl acetoacetate, but with some trouble. The best procedure was to first prepare ethyl normal propyl acetoacetate by Conrad's method,[1] using sodium ethylate, ethyl acetoacetate, and ethyl iodide, and to isolate and purify the reaction product. This is dissolved in two parts of benzene, and treated with one molecule of sodium, and when solution of the latter has taken place, with one molecule of methyl iodide at room temperature, the reaction mixture being allowed to stand a week or ten days. The benzene is distilled off, the sodium iodide extracted with water, the residue dried and distilled. At best, the yield is not very good, not over 60 per cent. of the theoretical.

3-Methyl-2-hexanone, $CH_3COCH(CH_3)CH_2CH_2CH_3$.—One molecule of ethyl methyl normal propyl acetoacetate was boiled for ten hours with four molecules of caustic potash in ten per cent. aqueous solution, and the resulting ketone distilled off with steam, the distillate separated, dried with calcium chloride and twice fractionated. The boiling point is 136–137°,[2] at 760 millimeters pressure. 190 grams of the acetoacetic ester derivative usually yielded between 40 and 50 grams of 3-methyl-2-hexanone. The analysis was satisfactory.

2,3-Dimethyl-2-hexanol, $CH_3C(OH)(CH_3)CH(CH_3)CH_2CH_2CH_3$.—A solution of methyl magnesium iodide was prepared by dissolving 12 grams of magnesium turnings in a mixture of 80 grams of methyl iodide and 80 grams of absolute ether. To this solution 57 grams of 3-methyl-2-hexanone mixed with an equal volume of absolute ether were gradually added, and the whole allowed to stand one hour, when the carbinol was set free by the customary treatment with water and hydrochloric acid. The ether layer was separated, dried over potassium carbonate, the ether distilled off, and the residue fractionated, which yielded 54

[1] Conrad and Limpach, *Ann.*, 192, 557.

[2] Jones, *Ann.*, 226, 293, gives the boiling point as 142°–147°.

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grams of 2,3-dimethyl-2-hexanol boiling at 150°–151° at 756 millimeters pressure. The analysis was satisfactory.

Properties: Colorless liquid, boiling at 150°–151° at 756 mm. pressure, with an odor something like that of musty apples. It is insoluble in water but miscible in all proportions with the common organic solvents.

Preparation and Reduction of 2,3-Dimethyl-2-iodohexane.—33 grams of 2,3-dimethyl-2-hexanol were mixed with 3.5 grams of red phosphorus and 32 grams of iodine were added to the mixture which was allowed to stand over night at room temperature, and then next day was heated for an hour at 80°. The resulting iodide was washed with water, filtered through asbestos to remove unchanged phosphorus and reduced in the following manner:

In a 250 cubic centimeter flask, fitted with a return condenser, about 200 grams of finely divided zinc[1] were placed and the flask was then immersed in a bath of cold water. The octyl iodide was introduced into the flask and was mixed with the zinc by thorough shaking. Concentrated (38 per cent.) hydrochloric acid was poured through the condenser tube until the flask was half full, when the apparatus was set aside and allowed to remain three days. The amount of octyl iodide was such that the zinc was almost covered by it, forming a sort of paste and the acid being cold, acted very slowly and on the zinc which was itself nearly covered by octyl iodide. The result was that the evolution of hydrogen, for the most part, took place at the surface of contact of the acid and octyl iodide, and the result was a very satisfactory reduction of the alkyl iodide to the hydrocarbon. At the end of three days, the layer of octane had collected above the aqueous solution and was separated, dried with calcium chloride and fractionated. The portion boiling at 110–115° was further purified as shown presently, while the residue which did not distil at 115° or above was put back into the reduction flask and the process repeated. The crude octane was purified in the usual manner by treating with concentrated sulfuric acid, shaking with potassium permanganate solution, and distilling over sodium, after which it was carefully fractionated, when about 10 grams of 2,3-dimethylhexane were obtained. The boiling point on the last fractionation was 113.8° to 114° at 760 millimeters pressure, but most of the fraction came over at the latter figure. The analysis was satisfactory.

Properties: Colorless, very mobil liquid, boiling at 113.8° to 114° at 760 millimeters pressure and possessing a characteristic rather strong odor. It has, at 15°, the specific gravity 0.7252 compared to water at 15°. The index of refraction was determined with the kind assistance of Mr. F. W. Barry and was found to be N_D (25°) = 1.4075.

[1] This had previously been treated with a few cubic centimeters of a dilute solution of copper sulfate.

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The above work was done in this laboratory during the year 1908–09. The research on the octanes will be continued and the brief comparison of the first eight given in this paper will be extended from time to time as each new series is completed.

I am deeply indebted to the C. M. Warren Fund for Research for much of the material used in this study.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

ON TRIPHENYLMETHYL.

[TWENTIETH PAPER.]

BY M. GOMBERG AND D. D. VAN SLYKE.[1]

Received February 27, 1911.

CONTENTS: 1. Introduction. 2. Synthesis of Materials. 3. Action of Molecular Silver on Ortho- and Para-halogenated Derivatives of Triphenylcarbinol Chloride. 4. Action of Silver Chloride on Orthobrominated Derivatives of Triphenylcarbinol Chloride in Sulphur Dioxide. 5. Action of Silver Sulfate on Ortho- and Para-halogenated Derivatives of Triphenylcarbinol Chloride; Inhibitive Effect of Sulfuric Acid upon the Action of Silver Sulfate; Structure of the Sulfates. 6. Summary.

1. Introduction.

In previous papers bearing on the constitution of triphenylmethyl and its many analogs the following facts of importance, among others, were brought out: (1) The triarylmethyls are capable of existing in two modifications—the colored and the colorless;[2] the colored form is not limited to the solid phase alone, but as has been shown by J. Schmidlin,[3] the two modifications exist in equilibrium with each other even when in solution. (2) In the colored modification one phenyl group has become apparently changed in its function, for in it the para position is extremely reactive and mobil, in strong contrast to the great stability of the three phenyl nuclei in triphenylmethane itself.[4] (3) A similarly striking change in the functions of one phenyl nucleus, simultaneously with the production of color and of salt-like properties in the compound itself, has been shown to take place when the colorless triphenycarbinol halides are dissolved in sulfur dioxide, or when the triphenylcarbinols—always colorless—are changed to the corresponding carbinol sulfates, always colored.[5]

The theoretical explanation which has been advanced in order to account for these newly acquired functions in the phenyl nucleus consists in attrib-

[1] This investigation was presented by Mr. Van Slyke to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *Ber.*, 34, 2729 (1901); 35, 2406 (1902); 37, 2036 (1904); 40, 1881 (1907).

[3] *Ibid.*, 41, 2471 (1908).

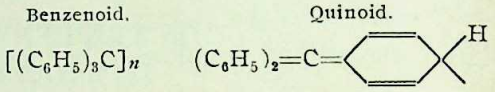
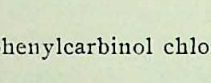
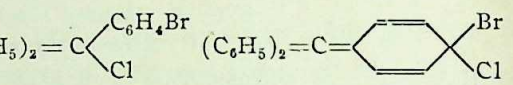
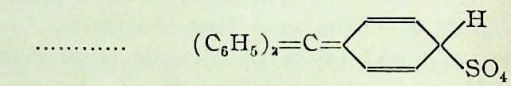
[4] *Ibid.*, 39, 3274 (1906).

[5] *Ibid.*, 40, 1847 (1907); 42, 406 (1909).

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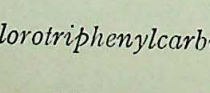
uting to that nucleus a tautomeric change from the benzoid to the para-quinoid state. With such a change the para-carbon atom would become in its character more like that in aliphatic than in aromatic compounds. Such an explanation accounts satisfactorily for the tremendous difference as regards the stability of the bromine in the para-brominated triphenylcarbinol halides according to whether we deal with the colorless solutions of the latter in benzene, chloroform, ether, etc., or with the colored solutions of the same compound in liquid sulfur dioxide. The following formulas illustrate the view-point.

	Benzenoid.	Quinoid.
Triphenylmethyl.....	$[(C_6H_5)_3C]_n$	
p-Bromotriphenylcarbinol chloride		
Triphenylcarbinol sulfate.....	.....	

The hypothesis as regards the existence of the two tautomeric forms of the triphenylmethane compounds has been since extended to the study of the xanthone and thioxanthone[1] derivatives. It was shown that there exists the closest analogy between these two classes of compounds on the one hand and the corresponding triphenylmethane compounds on the other, only that the former are far more prone towards tautomerization than the latter. It was further shown that the tautomeric colored salts obtainable from the xanthones and the thioxanthones must be considered, not as *oxonium* salts, but as *quinocarbonium* salts, just like their parent substances, the corresponding triphenylmethane derivatives.

The question now arises: Does ortho-quinoidation occur simultaneously with, or instead of, the para-quinoidation in the above mentioned instances of tautomerization. If it does, then the halogen placed in the ortho position should appear fully as reactive as it was found to be in the para position in the tautomerized products. On the other hand, if the ortho-halogen be found wholly inert then the conclusion appears justified as regards the non-occurrence of the ortho-quinoidation. This paper presents the results obtained in the attempt to answer the above question. The relative influence of chlorine and bromine in inducing tautomerization has also been studied, and there are also appended some further data in regard to the formation and behavior of the much-discussed triarylcarbinol sulfates.

2. Synthesis of Materials.

o-Chlorotriphenylcarbinol Chloride, 

[1] Gomberg and Cone, *Ann.*, 370, 142 (1909); 376, 183 (1910).

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o-Chlorotriphenylcarbinol, $(C_6H_5)_2C_6H_4Cl.C.OH$.—This product was synthesized by the action of ortho-chlorobenzoic ester on magnesium bromobenzene.

The ester was prepared from ortho-toluidine. The latter was diazotized according to Erdmann,[1] forming ortho-chlorotoluene. From the chlorotoluene, ortho-chlorobenzoic acid was prepared by oxidation with potassium permanganate.[2] For esterification, 1 molecule of dry sodium ortho-chlorobenzoate was heated for two hours at 160° with 1.1 molecules of dimethyl sulfate. The sodium methyl sulfate formed was dissolved in water, and the ester extracted with ether, dried over sodium sulfate, and distilled. The fraction boiling at 228–236° was equal to 80 per cent. of the theoretical amount.

For the Grignard reaction 4.1 g. (1 mol.) of magnesium were dissolved in an ethereal solution of 30 g. (1.1 mol.) of bromobenzene, and 12.5 g. (0.4 mol.) of ester added in ethereal solution. After two hours' boiling, the magnesium compound was decomposed with ice and hydrochloric acid. The ethereal extract was freed from bromobenzene by steaming, and the residue taken up in hot ligroin, boiled over charcoal and calcium chloride, then concentrated and allowed to crystallize. 11.8 g. of white carbinol were obtained melting at 91°. The pure recrystallized product melts at 95°.

Calculated for $C_{19}H_{15}Cl.O$:	C, 77.40; H, 5.13
Found:	C, 77.48; H, 5.60

o-Chlorotriphenylcarbinol Chloride.—11.8 g. of carbinol were dissolved in benzene, and the solution over calcium chloride saturated with hydrochloric acid. After standing some hours, the solution was concentrated, and on cooling 10 g. of white crystallin carbinol chloride, melting at 134–135°, crystallized. Melting point of pure product, 136°.

Calculated for $C_{19}H_{14}Cl_2$:	Hydrolyzable Cl, 11.33
Found:	Hydrolyzable Cl, 11.16.

o-Chlorotriphenylethoxymethane, $ClC_6H_4(C_6H_5)_2C.OC_2H_5$. — To a solution of 0.2 gram of sodium in absolute alcohol 2.3 g. carbinol chloride were added, and the solution boiled with reflux condenser for an hour. The sodium chloride was filtered out, and the solution concentrated. The product failed to crystallize in a freezing mixture or on standing for some time. After several weeks, crystallization occurred spontaneously, and 1.4 g. of a white product were obtained, melting at 77°. Easily soluble in ether, ligroin, alcohol, and benzene.

Calculated for $C_{21}H_{19}ClO$:	C, 78.12; H, 5.94.
Found:	C, 78.13; H, 6.13.

o-Chlorotriphenylanilidomethane, $ClC_6H_4(C_6H_5)_2C.NHC_6H_5$. — 3 g. car-

[1] *Ann.*, **272**, 145 (1893).
[2] *Ibid.*, **276**, 55 (1893).

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binol chloride were dissolved in about 20 cc. benzene and 2.2 g. redistilled aniline added. The anilide is not very soluble in benzene and it separated partially from solution along with the precipitated aniline hydrochloride. The anilide was extracted from the precipitate with hot benzene, and the benzene solution concentrated at room temperature. The product was obtained in 90 per cent. yield in the form of large, white crystals melting at 121°.

Calculated for $C_{25}H_{20}ClN$: N, 3.80.
Found: N, 4.11.

Unsymmetrical o-Chlorotetraphenylethane, $(ClC_6H_4)(C_6H_5)_2C - CH_2C_6H_5$. —This compound was prepared by the method of Gomberg and Cone.[1] 3 g. of carbinol chloride in dry benzene solution were added to an ethereal solution of twice the theoretical amount of benzyl-magnesium chloride. The condensation product separated out at once. The mixture was heated one-half hour on the water bath, then decomposed with dilute hydrochloric acid and ice. The ethereal extract, dried and concentrated, gave a product melting at 165°. Recrystallization from ligroin raised the melting point only to 165.5°. The product is most readily soluble in benzene, easily soluble in ether and warm ligroin, somewhat less so in alcohol.

Calculated for $C_{26}H_{21}Cl$: C, 84.64; H, 5.74.
Found: C, 84.66; H, 6.08.

o-Bromotriphenylcarbinol Chloride, $(C_6H_5)_2C\begin{matrix}C_6H_4Br(o)\\Cl\end{matrix}$.

This was prepared by the action of ortho-bromobenzoic ester on magnesium bromobenzene.

The ortho-bromobenzoic acid was prepared by diazotizing anthranilic acid in dilute sulfuric, and siphoning the diazonium solution into a mechanically agitated cuprous bromide suspension.[2] This gave us better yields (82 per cent. of the calculated) than diazotizing in the presence of cuprous bromide. A single recrystallization from water gave a pure product, melting at 150°.

The methyl ester was obtained by heating the dry sodium salt with methyl sulfate at 160° for two and a half hours, and isolating as in the case of the ortho-chlor ester. The yield was 87 per cent. of ester boiling at 245°–250°.

For synthesis of the carbinol chloride the ester was dissolved in absolute ether and added to a slight excess of phenyl magnesium bromide. After several hours' boiling, the product, which had separated as a gum, was decomposed with ice and dilute hydrochloric acid, and the resulting oily carbinol steamed to free it from bromobenzene. The carbinol was

[1] *Ber.*, 39, 1461 (1906).
[2] Graebe, *Ann.*, 276, 57 (1893).

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then dissolved in benzene, the solution boiled over charcoal and calcium chloride, and after filtration, saturated with dry hydrochloric acid in presence of fresh calcium chloride. On driving off the benzene and recrystallizing from ligroin, the carbinol chloride was obtained, the yield being 54 per cent. of the calculated.

Calculated for $C_{19}H_{14}BrCl$: Hydrolyzable Cl, 9.92.
Found: Hydrolyzable Cl, 9.82.

o-Bromotriphenylcarbinol, $(BrC_6H_4)(C_6H_5)_2C.OH$. — 2 g. of carbinol chloride were boiled in acetic acid solution. The carbinol was then precipitated by the addition of water, and taken up with ether. The ethereal extract was shaken with fresh portions of water until all the acetic acid was washed away. Concentration of the dried ethereal solution yielded 1.2 g. of pure white crystals. Recrystallized from ligroin the carbinol melts at 104°. It is easily soluble in benzene and ether, somewhat less so in alcohol and petroleum ether.

Calculated for $C_{19}H_{15}BrO$: Br, 23.58.
Found: Br, 23.18.

o-Bromotriphenylanilidomethane, $(BrC_6H_4)(C_6H_5)_2C.NHC_6H_5$. — 1.2 g. of aniline were added to 2 g. of carbinol chloride in benzene solution. After standing for two days, the solution was filtered from aniline hydrochloride, and concentrated by evaporation at room temperature. The product separated in pure white crystals, which were washed with ligroin, and dried *in vacuo*. Yield quantitative, 2.3 g. The anilide melts at 126°, is fairly soluble in hot petroleum ether and alcohol, slightly in cold; easily soluble in benzene.

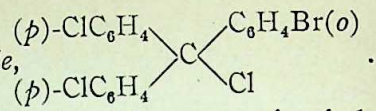
Calculated for $C_{25}H_{20}BrN$: N, 3.38.
Found: N, 3.63.

Unsymmetrical o-Bromotetraphenylethane, $(BrC_6H_4)(C_6H_5)_2C.CH_2C_6H_5$.— 2 g. of carbinol chloride dissolved in absolute ether were added to twice the theoretical amount of magnesium benzyl chloride. The mixture was boiled an hour, then decomposed with ice and dilute hydrochloric acid. The ethereal extract was concentrated and steamed, then taken up in petroleum ether, and dried over calcium chloride. From the concentrated solution the product separated in crystals, melting at 153°.

o-Bromotriphenylethoxymethane, $(BrC_6H_4)(C_6H_5)_2C.OC_2H_5$.—2 g. of carbinol chloride were dissolved in absolute alcohol, and added to an alcoholic solution of a slight excess of sodium. The mixture was boiled for an hour, then cooled and diluted with water. The ethoxy compound was extracted with ether, the ethereal solution dried and concentrated. The product refused to crystallize from ether or ligroin, but finally was obtained from alcohol in pure white crystals after several weeks' standing. Melting point 69–70°.

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o-Bromodi-p-chlorotriphenylcarbinol Chloride, 

—The product was prepared by the action of *p*-chloromagnesiumiodobenzene on ortho-bromobenzoic ester. The *p*-chloroiodobenzene required for the synthesis was prepared by diazotizing *p*-chloroaniline.[1]

1.1 molecules of magnesium were dissolved in an ethereal solution of one molecule of *p*-chloroiodobenzene and 0.9 molecule of ortho-bromobenzoic methyl ester added. After five hours' boiling the solution was decomposed as usual, and the dark, impure carbinol steamed, and then boiled in benzene solution with calcium chloride and charcoal. The filtered benzene solution was saturated with dry hydrochloric acid and, after several hours' standing over calcium chloride, concentrated *in vacuo*. Hot ligroin was added to the residue, and the entire mass crystallized while still warm. Like other derivatives of *o*-bromodi-*p*-chlorotriphenylmethane, it showed exceptional crystallizability. A 74 per cent. yield was obtained. The recrystallized product melted at 165°. The carbinol chloride is difficultly soluble in ligroin, soluble in chloroform and ether, very soluble in benzene.

Calculated for $C_{19}H_{12}Cl_3Br$: Hydrolyzable Cl, 8.31.
Found: Hydrolyzable Cl, 8.20.

o-Bromodi-p-chlorotriphenylcarbinol, $(BrC_6H_4)(ClC_6H_4)_2C.OH$.—3.4 g. of carbinol chloride were dissolved in 20 cc. of glacial acetic acid and boiled. The solution of the carbinol was poured into 200 cc. of water and the precipitated suspension extracted with ether. The extract was washed free of acid, dried over calcium chloride and concentrated. 2.6 g. of crystalline white carbinol was obtained, melting at 107°. The melting point was not changed by recrystallization from alcohol and ligroin successively. The substance is easily soluble in benzene and ether, fairly soluble in alcohol and ligroin.

Calculated for $C_{19}H_{13}Cl_2BrO$: Cl_2, 17.38; Br, 19.59.
Found: Cl_2, 17.44; Br, 18.80.

o-Bromodi-p-chlorotriphenylethoxymethane, $(BrC_6H_4)(C_6H_4Cl)_2C.OC_2H_5$.—2 g. carbinol chloride were dissolved in absolute alcohol and added to a solution of 0.14 g. (1.2 molecules) sodium in absolute alcohol. The solution was boiled for an hour, cooled, and poured into water. The suspended ethoxy compound was extracted with ether, the extract dried over sodium sulfate, and concentrated. 1 g. of ethoxy compound crystallized on cooling. Recrystallized twice from ligroin it melted at 108°. The product is readily soluble in benzene, ether and ligroin, less so in alcohol.

The ethoxy compound, peculiarly, melts at practically the same tem-

[1] Gomberg and Cone, *Ber.*, **39**, 3281 (1906).

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perature as the carbinol, although both were recrystallized until their melting points became constant. A mixture of the two, however, began to soften at 86°, and melted at 93°, showing conclusively their non-identity, which was confirmed by analysis.

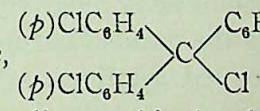
Calculated for $C_{21}H_{17}Cl_2BrO$: Cl_2, 16.27; Br, 18.33.
Found: Cl_2, 16.59; Br, 18.02.

o-Bromodi-p-chlorotriphenylanilidomethane, $(BrC_6H_4)(C_6H_4Cl)_2—C—NHC_6H_5$.—To 2 g. carbinol chloride in 20 cc. benzene solution was added 20 per cent. excess of aniline (1.1 g.) and the solution allowed to stand for a day. The anilide is unusually insoluble, and a considerable portion precipitated with the aniline hydrochloride. The latter was extracted with hot benzene and the extract united with the main solution. On concentrating at room temperature the anilide was obtained in almost quantitative yield, 2.0 g. It is difficultly soluble in all the usual solvents except hot benzene. When heated it turns green at 211° and melts to a dark liquid at 212°.

Calculated for $C_{25}H_{18}Cl_2BrN$: N, 2.90.
Found: N, 2.94.

Unsymmetrical o-bromodi-p-chlorotetraphenylethane, $(BrC_6H_4)(C_6H_4Cl)_2C—CH_2C_6H_5$.—This was obtained by the same method as described for the other unsymmetrical tetraphenylethanes. Recrystallized from alcohol it melts at 162°. The substance is readily soluble in benzene, less so in ether and ligroin, and is fairly insoluble in alcohol, from which it can be recrystallized almost quantitatively.

Calculated for $C_{26}H_{19}Cl_2Br$: Cl_2, 14.71; Br, 16.59.
Found: Cl_2, 14.78; Br, 16.19.

p-Bromodi-p-chlorotriphenylcarbinol Chloride,  .

—This product was made from the corresponding carbinol, which was prepared by the Grignard reaction. 2.29 g. magnesium were dissolved in an ethereal solution of 24.4 g. (1.1 molecules) of *p*-chloroiodobenzene. To the solution was added 10.1 g. (1 molecule) of *p*-bromobenzoic methyl ester, and the mixture boiled six hours. It was decomposed as usual, and the product, after steaming off the excess of *p*-chloroiodobenzene, taken up in ether and boiled under reflux condenser with calcium chloride and charcoal. The colorless carbinol crystallized from the concentrated solution, and was washed with ligroin. The product recrystallized twice from petroleum ether melts at 106°. Yield, 12 g. which is 65 per cent. of the calculated amount.

Calculated for $C_{19}H_{13}Cl_2BrO$: Cl_2, 17.38; Br, 19.59.
Found: Cl_2, 17.68; Br, 19.05.

The carbinol chloride obtained by the action of hydrochloric acid on

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the above carbinol and melting at 122° has already been described by Gomberg.[1]

p-Bromodi-p-chlorotriphenylethoxymethane, $(BrC_6H_4)(C_6H_4Cl)_2C.OC_2H_5$.—The ethoxy compound was prepared similarly to the corresponding *o*-bromo derivative as described above. Recrystallized from ether the substance melts at 188°. The substance is soluble in benzene, moderately soluble in ether, comparatively insoluble in alcohol.

Calculated for $C_{21}H_{17}Cl_2BrO$:	Cl_2, 16.27; Br, 18.33.
Found:	Cl_2, 16.65; Br, 18.07.

p-Bromodi-p-chlorotriphenylanilidomethane, $(BrC_6H_4)(C_6H_4Cl)_2C.NHC_6H_5$.—This anilide was obtained similarly to the above-described anilides. Recrystallized from a mixture of benzene and petroleum ether, the product on heating turns green at 178° and melts at 182°. It is soluble in benzene, fairly soluble in ether, insoluble in alcohol and ligroin.

Calculated for $C_{25}H_{18}Cl_2BrN$:	N, 2.90.
Found:	N, 2.92.

The synthesis of the di- and of the tri-ortho-chlorotriphenylcarbinol chlorides was attempted by the Grignard reaction but the reaction, when it took place at all, furnished such unsatisfactory yields of the desired products that the preparation of these compounds was given up for the present.

3. Action of Molecular Silver on ortho- and para-Halogenated Derivatives of Triphenylcarbinol Chloride.

When para-halogenated derivatives of triphenylcarbinol chloride in benzene solution are shaken with an excess of molecular silver, not only the carbinol chlorine is removed, but part of the para-nuclear halogen as well, indicating the quinoid nature of the triphenylmethyl analogs in the brilliantly colored solutions. Approximately one-half of an atom of para-halogen was removed when one such atom was present, three-fourths when there were two para-halogens, seven-eighths when there were three. Gomberg[2] explained this by the hypothesis that the reaction products successively couple together as they are formed, with elimination of an atom of para-halogen from each complex at each coupling, on the assumption that in solution triphenylmethyl exists partially in the quinol state as suggested by Jacobson, $(C_6H_5)_2C = C_6H_4\begin{matrix}H\\ \diagup\\ \diagdown\\ C(C_6H_5)_3\end{matrix}$. The theoretical amount of para-halogen removable in this manner should be one-half, three-fourths, or seven-eighths of an atom for each original molecule of carbinol chloride, according as the latter possesses one, two, or three atoms respectively of para-halogen. The requirements of the

[1] *Ber.*, 40, 1863 (1907).
[2] *Ibid.*, 40, 1886 (1906).

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theory were thus found to harmonize in a remarkably close way with the results obtained.

The present experiments were undertaken in order to obtain experimental data from derivatives containing both para-bromine and para-chlorine in the same molecule, and to ascertain from ortho-halogenated derivatives whether evidence could be obtained of ortho-quinoid formation. 0.3 to 0.5 g. portions of the carbinol chlorides tabulated below were sealed with benzene and 1.5 to 2.5 g. portions of molecular silver; the tubes were then shaken at room temperature for several months and their contents analyzed.

TABLE I.—ACTION OF MOLECULAR SILVER ON ORTHO- AND PARA-HALOGENATED DERIVATIVES OF TRIPHENYLCARBINOL CHLORIDE.

No.	Carbinol chloride.	Days shaken with silver.	Carbinol chlorine. Per cent. Found.	Carbinol chlorine. Per cent. Calculated.	Ring chlorine. Found. Per cent.	Ring chlorine. Found. Atoms.	Ring chlorine. Per cent. calculated. 1 atom.	Ring bromine. Found. Per cent.	Ring bromine. Found. Atoms.	Ring bromine. Per cent. calculated. 1 atom.	Total ring halogen. Atoms.
1	*o*-chloro	106	11.15	11.34	0.00	0.00	11.34	..	...	...	0.00
2	*o*-bromo	222	8.98	9.92	..	...	...	0.00	0.00	22.37	0.00
3	*o*-bromodi-*p*-chloro	206	8.31	8.31	5.90	0.711	8.31	0.00	0.00	18.75	0.711
4	*o*-bromodi-*p*-chloro	206	8.31	8.31	6.05	0.728	8.31	0.00	0.00	18.75	0.728
5	*p*-bromodi-*p*-chloro	198	8.31	8.31	3.31	0.398	8.31	5.74	0.307	18.75	0.706
6	*p*-chlorodi-*p*-bromo	157	7.53	7.53	2.17	0.288	7.53	9.22	0.542	16.98	0.830
7	*p*-chlorodi-*p*-bromo	157	7.53	7.53	2.17	0.288	7.53	9.76	0.575	16.98	0.863

The conclusions afforded by the above results may be summarized as follows:

1. The results of numbers 1, 2, 3, and 4 show that no trace of ortho-halogen was removed in any case. There is no indication of the formation of ortho-quinoid nuclei.

2. The total amounts of para-halogen removed, as related to the number of para-halogen atoms present, agree (except No. 5, which is too low, probably from experimental error) with those of Gomberg and Cone mentioned above, and substantiate strongly the explanation given for the reaction and based upon successive coupling of the products.

3. Bromine in the para-position is somewhat more reactive towards molecular silver than is chlorine. A larger portion of a bromine atom is removed in Nos. 6 and 7 than of chlorine in No. 5; also of bromine in No. 5 than of chlorine in Nos. 6 and 7.

Comparative Influence of Halogen in Ortho and Para-positions upon Color caused by the Action of Molecular Silver upon Halogenated Triphenylcarbinol Chlorides.—The solutions contained 0.3 to 0.5 g. carbinol chloride dissolved in 12–15 cc. benzene and sealed in tubes with the molecular

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silver, free from all traces of air. The derivatives are arranged in pairs differing, except in the last, only in the position of the halogen atoms, so that the comparative effect of halogen in the ortho and para positions is clearly brought out.

TABLE II.

Substance.	Color caused by action of silver.
Triphenylcarbinol chloride	Deep yellow
Mono-*p*-chlorotriphenylcarbinol chloride	Light red
Mono-*o*-chlorotriphenylcarbinol chlordie	Deep red
Mono-*p*-bromotriphenylcarbinol chloride	Brown-red
Mono-*o*-bromotriphenylcarbinol chloride	Deep red Tinge purple
Mono-*p*-bromodi-*p*-chlorotriphenylcarbinol chloride	Orange
Mono-*o*-bromodi-*p*-chlorotriphenylcarbinol chloride	Deep purple
Di-*p*-bromotriphenylcarbinol chloride	Orange
Di-*o*-chlorotriphenylcarbinol chloride	Deep violet
Mono-*p*-chlorodi-*p*-bromotriphenylcarbinol chloride	Orange

The greater influence of the ortho-halogen substitutents in deepening the color is apparent, especially in the di- and tri-halogenated compounds. The para derivatives give colors varying from orange to red, the ortho from red to purple and violet. The similarity in the greater influence of ortho substituents in the analogs of triphenylmethyl and in the malachite green derivatives as observed by Noelting[1] indicates a similar structural cause of color.

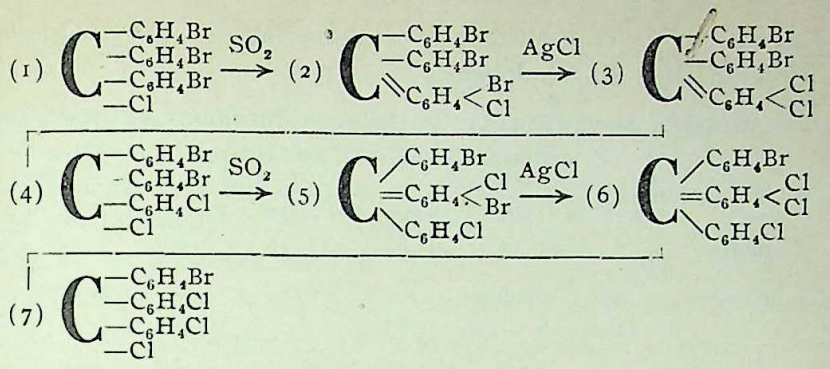
4. Action of Silver Chloride on ortho-Brominated Derivatives of Triphenylcarbinol Chloride.

When tri-*p*-bromotriphenylcarbinol chloride is dissolved in sulfur dioxide and shaken with silver chloride the three bromine atoms are successively replaced by chlorine. The carbinol chloride in solution is at least partially in the quinoid form, an equilibrium existing, when part of the bromine has been replaced, between molecules containing brominated nuclei in the quinoid state and those in which a chlorinated nucleus is the quinoid one. The silver chloride reacts with the former, the disturbance of the equilibrium resulting in the shifting of the quinoidation to fresh bromine-containing nuclei as those formerly brominated become chlorinated. The replacement of bromine by chlorine consequently continues until it is complete, whether one, two, or three para-bromine atoms are present at the start. In the following diagram is shown the mechanism covering the replacement of the first two bromine atoms only, assuming, as we may, an equilibrium between products (3) and (4), and also between products (6) and (7).

[1] *Ber.*, 39, 2041 (1906).

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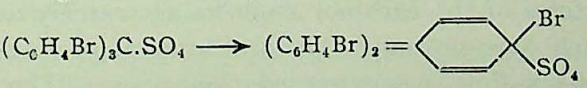


As will be shown by experiments with the sulfates described below, (p. 542) para-bromine exerts a stronger influence than chlorine in directing the quinoidation towards the nucleus in which it is situated. Even when there are two para-chlorine atoms to one bromine the quinoidation takes place almost entirely in the brominated nucleus.

We have now tested the ability of sulfur dioxide to induce ortho as well as para quinoidation. 0.3 g. portions of ortho-bromo- and ortho-bromodi-*p*-chlorotriphenylcarbinol chloride were sealed in bomb tubes with sulfur dioxide and 0.6 g. portions of silver chloride. The tubes were shaken one month at 20° and one month at 50°. *No silver bromide was formed in either case.* The tautomerization resulting from the influence of the solvent on a carbinol chloride cannot apparently be influenced by ortho-halogen, even bromine, to form ortho-quinoid nuclei.

5. Action of Silver Sulfate on ortho- and para-Halogenated Derivatives of Triphenylcarbinol Chloride.

The first action of silver sulfate on para-brominated triphenylcarbinol chloride is to remove the aliphatic chlorine attached to the central carbon atom, with formation of intensely colored neutral sulfates of the triphenylmethyl radicle. The second step in the reaction is the removal of one—and no more—para-bromine atom from each triphenylmethyl radicle. This removal can only be explained on the assumption that the sulfates undergo tautomerization at the moment of their formation and consequently have a quinoid nucleus as represented below, because the halogen in benzoid rings is absolutely inert towards silver salts.



The experiments tabulated below were undertaken in order to ascertain the comparative influence of chlorine and bromine in directing the quinoidation to or from the rings in which the halogens are substituted, and further to test the possibility of ortho-quinoid formation. The silver sulfate (1.5 to 2.5 g.), carbinol chloride (0.3 to 0.5 g.), and methyl sulfate as a solvent were sealed in a tube and shaken mechanically in a

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thermostat at 40°. The different carbinol chlorides are designated by the positions of their ring halogens.

TABLE III.—ACTION OF SILVER SULFATE ON CARBINOL CHLORIDES IN METHYL SULFATE.

No.	Carbinol chloride.	Days shaken.	Carbinol chlorine removed. Calculated.	Carbinol chlorine removed. Found.	Ring chlorine removed. Calculated.	Ring chlorine removed. Found	Ring bromine removed. Calculated.	Ring bromine removed. Found.
1	Mono-*o*-chloro-	7	11.32	10.84	11.32	0.00	...	...
2	Mono-*o*-bromo-	3	9.92	9.82	...	..	22.37	0.00
3	" "	11	9.92	9.65	...	..	22.37	0.00
4	*o*-Bromodi-*p*-chloro-	2/3	8.31	8.31	8.31	7.72	18.75	0.00
5	" "	3 1/2	8.31	8.31	8.31	8.17	18.75	0.00
6	" "	5	8.31	8.31	8.31	8.28	18.75	0.00
7	" "	10	8.31	8.31	8.31	8.24	18.75	0.00
8	" "	13	8.31	8.31	8.31	8.35	18.75	0.00
9	*p*-Bromodi-*p*-chloro-	9	8.31	8.31	8.31	0.25	18.75	16.03
10	" "	11	8.31	8.31	8.31	0.80	18.75	15.92
11	" "	19	8.31	8.31	8.31	0.00	18.75	16.46
12	" "	26	8.31	8.31	8.31	0.77	18.75	15.34
13	*p*-Chlorodi-*p*-bromo-	6	7.53	7.53	7.53	0.04	16.98	16.83
14	" "	14	7.53	7.53	7.53	0.10	16.98	16.89

The solutions all became deep red at once upon shaking with silver sulfate, the substances containing ortho-halogen giving a deeper color, almost black, than those with only para-halogen. The "ring chlorine" was estimated by subtracting the theoretical carbinol chlorine from the total. The bromine was estimated, as usual, by igniting the mixed halides in chlorine gas.

From the data presented we may draw the following conclusions:

1. When bromine and chlorine occupy para-positions in different nuclei of the same substance, the bromine is removed in preference to the chlorine. When one bromine and two chlorine atoms occupy the para-positions (Nos. 9–12) not more than a tenth of an atom of ring-chlorine is removed, while nearly nine-tenths of the single atom of bromine is taken out. When there are two para-bromines to one para-chlorine (Nos. 13–14) an atom of bromine is taken out quantitatively, the amount of chlorine in excess of the carbinol atom being scarcely above the limit of error. In each case, however, the total amount of ring-halogen taken out by the silver sulfate never exceeds one atom. The para-bromine atom consequently influences the quinoid transformation, occurring when a sulfate is formed, strongly towards the nucleus which contains the bromine.

2. No ortho-quinoid rings are formed in the colored sulfates. Even when an ortho-bromine atom is the only halogen in the three nuclei (Nos. 2 and 3), in which case it would presumably exert a strong influ-

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ence towards the formation of an ortho-quinoid ring, if such were possible, not the slightest trace of bromine is removed. When in addition to the ortho-bromine in one nucleus there are para-chlorines in the other two (Nos. 4–8), one atom of para-chlorine is removed quantitatively, showing that in the ortho position bromine completely loses its influence to direct the quinoidation towards its own nucleus.

A series of experiments was also carried out with sulfur dioxide instead of methyl sulfate as a solvent. The results obtained agree with the preceding, in showing that one para-halogen atom is removed from the colored neutral sulfate but that ortho-halogen is untouched.

Inhibitive effect of sulfuric acid upon removal of para-halogen from colored sulfates by silver sulfate.

It was found, in the case of the *p*-bromodi-*p*-chloro- and *o*-bromodi-*p*-chloro-sulfates, as by Gomberg in the cases of the *p*-bromo-and tri-*p*-bromo-sulfates, that the presence of slight amounts of free sulfuric acid in the methyl sulfate reaction mixture protects the para-halogen from removal by silver sulfate.

In the experiments tabulated below 0.3 g. portions of carbinol chloride with 1.5 g. portions of silver sulfate were weighed into test tubes, 10 cc. of methyl sulfate and the indicated amount of sulfuric acid then added, and the tube at once sealed and placed on the shaker at 50°. The results of Table IV were obtained after nineteen days' shaking.

TABLE IV.—INHIBITIVE EFFECT OF SULFURIC ACID ON REMOVAL OF PARA-BROMINE BY SILVER SULFATE FROM *p*-BROMODI-*p*-CHLOROTRIPHENYLCARBINOL SULFATE.

No.	Molecules sulfuric added per 1 mol. carbinol chloride.	Per cent. bromine removed.	Calculated 1 atom of bromine.
1	0	16.46	18.75
2	$^1/_2$	10.77	18.75
3	1	1.32	18.75
4	2	0.13	18.75

From the *o*-bromodi-*p*-chlorocarbinol chloride an atom of para-chlorine is quickly and quantitatively removed in the absence of sulfuric acid. But here again in the presence of acid, the action of silver sulfate is greatly hindered. The effect of time of reaction as well as that of the amount of acid was studied in this case.

TABLE V.—EFFECT OF AMOUNT OF SULFURIC ACID AND DURATION OF REACTION ON AMOUNT OF PARA-CHLORINE REMOVED BY SILVER SULFATE FROM *o*-BROMODI-*p*-CHLOROTRIPHENYLCARBINOL SULFATE.

Molecules sulfuric acid added per 1 mol. carbinol chloride.	Percentage of para-chlorine removed.			Calculated, 1 atom.
	16 hrs.	3½ days.	10 days.	
0	7.72	8.17	8.24	8.31
$^1/_2$	7.36	7.21	7.72	8.31
1	5.24	6.40	7.08	8.31
2	1.13	2.72	3.30	8.31

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It is apparent that there is no simple ratio between the amount of sulfuric acid added and the amount of para-halogen protected. But it is equally apparent that the inhibitive effect of sulfuric acid is much smaller in case of chlorine than in case of bromine in the para position.

Tri-p-halogen Acid Sulfates.

Baeyer[1] obtained by the action of concentrated sulfuric acid upon an excess of carbinol in solution brown crystallin sulfates of tri-*p*-chloro- and tri-*p*-iodo-triphenylcarbinol. The sulfates showed a green metallic luster, and were of the constitution $(R_3C)SO_4H.H_2SO_4$. Gomberg[2] prepared similar sulfates of tri-*p*-chloro- and tri-*p*-bromocarbinol, using methyl sulfate instead of chloral as a solvent, the methyl sulfate having the marked advantage of being a solvent for sulfuric acid. Prepared with methyl sulfate, the products were found to contain not one molecule of excess sulfuric acid, as Baeyer's results indicated, but from $1^1/_2$ to 2 molecules.

The ortho-bromodi-*p*-chlorosulfate could not be brought to crystallize, but the *p*-bromodi-*p*-chlorocarbinol gave by Gomberg's method a beautifully crystallin sulfate with green metallic luster, the yield being about 80 per cent. of the calculated amount. If the sulfuric acid solution in methyl sulfate was added to a cold benzene methyl sulfate solution of the carbinol, the carbinol sulfate usually separated quickly in fine crystals, while if the solution was warm, crystallization occurred slowly, with formation of large, compact crystals, in form suggestive of cubical salt crystals. The analyses gave compositions similar to those of Gomberg's polysulfates, the percentage of (SO_4) varying from that corresponding to $(R_3C)SO_4H.1^1/_2H_2SO_4$ to that corresponding to $(R_3C)SO_4H.2H_2SO_4$. Either the substance is a mixture of the sulfates containing, respectively, one and a half and two extra molecules of sulfuric acid, or, as seems more probable, it contains two extra molecules of sulfuric acid, the analysis falling low because of the readiness with which the sulfate hydrolyzes, even by short contact with air.

The polysulfate containing three molecules of sulfuric acid, from *p*-bromodi-*p*-chlorotriphenylcarbinol, was dissolved in both methyl sulfate and sulfur dioxide, and both solutions shaken two months at 50° with silver sulfate. The residue from the methyl sulfate tube gave too slight an amount of silver halide for estimation, although it could be qualitatively determined. That from the sulfur dioxide gave an amount of silver halide corresponding only to 0.37 per cent. of bromine.

It is clear from the above results that these acid sulfates, unlike the normal sulfates, do not give up their para-halogen on treatment with

[1] *Ber.*, 38, 1162 (1905).
[2] *Ibid.*, 40, 1853 (1907).

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silver sulfate, although every precaution has been taken to insure against the possible reverse tautomerization to the benzenoid form during the treatment with the silver salt. Similar negative results with the acid sulfates, obtained by Baeyer previously in point of time to the positive results on the normal sulfates as described by one of us, led Baeyer to the conclusion that these, and also all the other similarly colored salts are not quinoid in constitution. Baeyer's conclusion based, as it is, on evidence of negative nature only, does not seem to us warranted. Certainly it is not warranted as regards the colored carbinol chlorides or the normal sulfates, the quinoid nature of which has been inferred from results of strictly positive character.

We have shown that the normal sulfates, like the colored carbinol chlorides, contain a labil para-halogen and consequently, like the latter, must be quinoid. It has been further shown that in these very same sulfates the para-halogen becomes partially protected against the action of silver salt by the presence of free sulfuric acid, and the protection becomes almost complete when the relative concentration of the free acid is equal to two molecules. The action of the free acid upon the normal sulfates consists primarily, no doubt, in the formation of acid sulfates. Does the acid at the same time induce the tautomerization of the active quinoid to the non-reactive benzenoid form, and this without change of color? Such an inference as regards the action of sulfuric acid is entirely contrary to what we know of the action of hydrochloric acid. Gomberg and Cone[1] have demonstrated that certain normal, colorless carbinol chlorides of this series are converted by excess of hydrochloric acid into acid chlorides which are colored and are quinoid. It does not seem reasonable to assume that sulfuric acid would act in the very opposit direction from that in which hydrochloric acid acts. Consequently the non-reactivity of the para-halogen in the acid sulfates must find its explanation in some hypothesis which would still admit of a structural analogy between the normal and the acid sulfates.

Some years ago, soon after the publication of Baeyer's negative results with the acid sulfate, Stieglitz and Barnard[2] have made the suggestion that the non-activity of these acid sulfates can still be reconciled with their having a quinoid constitution, if we assign to them the constitution I as "chloronium" or "bromonium" salts.

$(BrC_6H_4)_2C:C_6H_4:Br.OSO_3H$ I. $(C_6H_5)_2C:C_6H_4:H.OSO_3H$ II.

Baeyer criticized this interpretation because on the basis of this view, in the salts obtainable from carbinols which contain in place of the para-halogen some other group, that group, or even the para-hydrogen itself

[1] *Ann.*, 370, 142 (1909).

[2] THIS JOURNAL, 27, 1016 (1905).

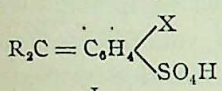
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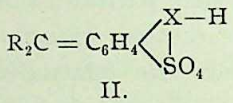
must likewise become basic and trivalent (Formula II).[1] We believe, however, that the kernel of Stieglitz and Barnard's view is none the less correct. So modified as to meet Baeyer's criticism, that interpretation furnishes a most satisfactory and plausible explanation of the entire behavior of these salts.

Structure of the Sulfates.

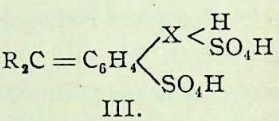
The normal sulfates must be considered as quinoid and on that basis can have only one possible constitution as given on page 541. The partial protection of the para-halogen in the mono-acid and the complete protection in the poly-acid sulfates is most rationally explained by assuming a structural connection between the para quinoid halogen and the combined acid radicles. The structure of the mono-acid sulfates may be represented as I or II, and that of the poly-acid sulfates as III, where x = halogen.



I.



II.



III.

The halogen thus assumes in II the trivalent condition, as in chlorites bromites, and in iodonium compounds, and in III perhaps even a higher valence, as in chlorates and bromates. The halogen, having become trivalent, has changed its properties, and is no more capable of precipitation by silver than the chlorine in the chlorate or in some of the complex inorganic double salts of Werner that contain non-ionizable halogen. Such halogen we will term, after the iodonium compounds, bromonium or chloronium.

For the polysulfates only the bromonium or the chloronium formula III applies. It expresses the chromatic nature of these substances as well as the complete protection of the para-halogen from the action of the silver salts. For the nono-acid sulfates, present results indicate that both I and II apply, I being in considerable evidence when the para-halogen is chlorine, II almost the exclusive form when the para-halogen is bromine; *i. e.*, bromine shows much greater tendency to assume the bromonium form than does chlorine to assume the chloronium. This relative tendency of the two halogens is in harmony with our knowledge as regards the basicity of iodine in the iodonium compounds. The probability that para-chlorinated mono-acid sulfates are largly of form I follows from the fact that the greater part of their halogen appears unprotected. Table V (p. 543) shows that the addition of one molecule of sulfuric acid to the normal sulfates—a little more than sufficient to form the mono-acid sulfate—does not protect the greater part of the para-chlorine. This seems still more evident when one compares Table V with Table

[1] *Ber.*, 40, 3083 (1907).

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IV. The latter shows that a molecule of acid under the same conditions almost completely protects the para-halogen when the latter is bromine. Gomberg's results with mono-*p*-bromo- and tri-*p*-bromocarbinol chlorides are similar.

The following experiments show more definitly the inertness of para-bromine in a para-brominated *mono*-acid sulfate. One molecule of sulfuric acid, just enough to form the mono-acid sulfate, was dissolved in methyl sulfate as a solvent with one molecule of mono-*p*-bromotriphenylcarbinol chloride, and the liberated hydrochloric acid driven off with dry carbon dioxide, until the carbinol chlorine was almost quantitatively removed. The carbinol chloride was thus changed to acid sulfate, R_3CSO_4H. To the solution of the organic sulfate was now added an excess of silver sulfate and the mixture sealed off and shaken for thirty days at 50°. 0.036 atom of chlorine was obtained, corresponding nearly to the slight amount of carbinol chlorine not driven off by the previous treatment with sulfuric acid, but no bromine whatever could be detected. In a similar experiment with the *p*-bromodi-*p*-chlorotriphenylcarbinol chloride less than 0.1 atom of bromine was freed. It is, therefore, apparent that all the para-bromine in mono-acid sulfates is protected, a fact which is explainable on the basis of structure, the para-brominated mono-acid sulfates having almost entirely the bromonium structure II.

The Action of Sulfuric Acid upon Triphenylcarbinol Chlorides.

In order to gain some idea as to the avidity with which the sulfuric acid is held in the bromonium salts the following set of experiments was carried out. Exactly one molecule of sulfuric acid was allowed to act upon two molecules of various triarylcarbinol halides. In case of the simple triphenylcarbinol chloride the reaction may be expected to proceed in these two steps:

$$(a) \qquad R_3C.Cl + H_2SO_4 = R_2C : C_6H_4 < \begin{matrix} H \\ SO_4H \end{matrix} + HCl.$$

$$(b) \quad R_2C : C_6H_4 < \begin{matrix} H \\ SO_4H \end{matrix} + R_3C.Cl = \left(R_2C : C_6H_4 < H\right)_2SO_4 + HCl.$$

But in case of para-halogenated carbinol halides the presumption is that reaction (*b*) will be almost entirely absent, because of the salt-like nature of the chloronium or the bromonium sulfates which have resulted in reaction (*a*). In other words, on the basis of this structure, para-halogenated carbinol halides can yield only one mol. of hydrochloric acid, while the non-halogenated carbinol halides can yield under identical conditions twice as much hydrochloric acid.

The method of experiment adopted to determin the amount of carbinol chloride reacting with sulfuric acid was to determin the amount of hydrochloric acid freed in this reaction. The carbinol halide (2 mols.)

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and sulfuric acid (1 mol.) were dissolved in carefully purified methyl sulfate, the solution was gently heated to 40–50°, and the liberated hydrochloric acid was driven out by a stream of dry carbon dioxide, the gas passing through a standard silver nitrate solution. Preliminary experiments with definit amounts of hydrochloric acid dissolved in methyl sulfate proved the method to be reliable.

The results of these experiments point unmistakably to a very marked difference in the behavior of the acid sulfate of non-halogenated carbinols on the one hand and those containing para-halogen on the other. With triphenylcarbinol chloride treated as above outlined, 1 mol. of sulfuric acid liberates readily the first mol. of hydrochloric acid (equation *a*) and somewhat more slowly the second (equation *b*), the whole process being completed in less than two days. But with para-bromo- and with di-*p*-bromotriphenylcarbinol halides, even on seven days' continuous treatment, no more than 1.3 mol. of hydrochloric acid was liberated, a result harmonizing well with the bromonium structure of the acid sulfate, wherein the acid is held in combination by the halogen.

6. Summary.

1. A number of new halogenated derivatives of triphenylmethane have been synthesized.

2. When the halogenated carbinol chlorides were treated with molecular silver, forming halogenated analogs of triphenylmethyl, the solutions obtained with ortho-halogenated derivatives were distinguished for depth and brilliancy of color.

3. When derivatives of triphenylcarbinol chloride containing para-halogen in two or three nuclei were dissolved in benzene and the solution shaken for three or more months with molecular silver, it was observed that: (*a*) a portion of each atom of such para-halogen was removed; (*b*) the total amount of para-halogen removed corresponded to about three-fourths atom when two para-halogen atoms were present, seven-eighths when three were present. Theses results substantiate the views of Gomberg concerning the quinoid structure of triphenylmethyl and its halogenated analogs in their colored solutions.

4. The conclusion of Gomberg, drawn from results obtained with normal *p*-bromo- and tri-*p*-bromotriphenylmethyl sulfates, that the colored triphenylmethyl sulfates have quinoid structure, is substantiated by further experimental evidence: One para halogen atom, and only one, becomes unstable, and can be readily removed by further action of the silver.

5. When one or two nuclei contain bromine, the other nucleus or nuclei chlorine, in the para position, the quinoidation of the sulfate in methyl sulfate solution takes place almost entirely in the brominated nuclei.

6. The para-halogen in the mono- and in poly-acid sulfates, unlike

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that in the neutral sulfates, cannot be removed by the action of silver sulfate. The protection of the halogen by the sulfuric acid is explained on the ground that in the acid sulfates the sulfuric acid is combined directly with the para-halogen of the quinoid nucleus. The explanation is supported by data resulting from observation both of the inhibitive effect of sulfuric acid upon the reaction between para-halogenated carbinol chlorides and silver sulfate, and of the nature of the reaction between sulfuric acid and carbinol chlorides alone.

7. No evidence of the formation to the slightest degree of the ortho-quinoid nuclei could be obtained by experiments with ortho-brominated derivatives, either with the neutral sulfates by means of silver sulfate, or with the carbinol chlorides in sulfur dioxide solution on treatment with silver chloride, or in the triphenylmethyl analogs on treatment with molecular silver. Apparently only para-quinoid rings are formed.

ANN ARBOR, MICH.

[FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE SULFUR REQUIREMENTS OF FARM CROPS IN RELATION TO THE SOIL AND AIR SUPPLY.[1]

BY E. B. HART AND W. H. PETERSON.

Received January 2, 1911.

Preliminary to a special investigation on the relation of the form and supply of sulfur in feeds to wool production, it was necessary to determin the total sulfur in a number of our common crop materials. The results secured led to a further consideration of the question of the adequacy of the natural sources of supply of this element for continuous crop production and the data relating to that problem are presented in this paper.

It is generally recognized to-day by agricultural chemists that the amount of sulfur in plant materials, as determined in the ash, is in most cases entirely too low; that in the process of ashing, sulfur is lost and the residual amount found in the ash may represent but a fraction of that originally present in the plant tissue. Such losses of sulfur by ignition have been the subject for study by a number of investigators. Contributions to this phase of the question have been made by Berthelot,[2] Barlow,[3] Fraps,[4] Goss,[5] Beistle,[6] Sherman,[7] and others. The work of

[1] Published with permission of the Director of the Wisconsin Experiment Station, University of Wisconsin.

[2] *Compt. rend.*, 128, 17.

[3] THIS JOURNAL, 26, 341 (1904).

[4] Reports of N. C. Experiment Station, 1901–1903.

[5] New Mexico Experiment Station, *Bull.*, 44.

[6] THIS JOURNAL, 24, 1903.

[7] *Ibid.*, 24, 1100.

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these several investigators has served to emphasize the inaccuracy of determining the total sulfur of plant tissue by an estimation of that element in the ash.

For the purpose of our work a large number of total sulfur determinations have been made on our common farm products by the peroxide method, as outlined by Osborne.[1]

Amounts of Sulfur Trioxide in Feeding Materials.

The results secured by the Osborne method are reported in Table I. All determinations were made on the air-dried materials. For convenience of reference the results are reported both as elemental sulfur and as sulfur trioxide, although in our discussion of the subject the latter formula for expressing the amount of sulfur will be used. In addition to the total amounts of sulfur trioxide reported there are given in a number of cases the amounts contained in the ash as secured by Wolff.

TABLE I.—SULFUR IN FEEDING STUFFS—AIR-DRY.

Material.	Sulfur. Per cent.	Sulfur trioxide. Per cent.	Sulfur trioxide in ash.[2] Per cent.
Alfalfa hay	0.287	0.717	0.425
Alfalfa seed	0.292	0.730	...
Barley	0.153	0.382	0.060
Barley straw	0.147	0.367	0.207
Beans (white garden)	0.232	0.580	0.130
Buckwheat	0.136	0.341	...
Cabbage	0.819	2.047	1.317
Clover, red	0.164	0.410	0.222
Cornmeal, white	0.170	0.425	0.010
Cornmeal, yellow sample 1	0.139	0.347	...
Cornmeal, yellow sample 2	0.139	0.347	...
Corn stover, sample 1	0.126	0.315	0.282
Corn stover, sample 2	0.116	0.290	...
Corn stover, sample 3	0.115	0.287	...
Corn stover, sample 4	0.128	0.320	...
Corn silage	0.122	0.305	...
Cottonseed meal	0.487	1.217	0.092
Flour, wheat	0.180	0.450	...
Flour, graham	0.183	0.457	...
Gluten feed, sample 1	0.560	1.399	...
Gluten feed, sample 2	0.500	1.249	...
Hay, mixed	0.160	0.400	0.354
Linseed meal, sample 1	0.404	1.010	0.190
Linseed meal, sample 2	0.375	0.937	...
Oats, sample 1	0.189	0.472	0.055
Oats, sample 2	0.180	0.450	...
Oatmeal, sample 1	0.223	0.557	...
Oatmeal, sample 2	0.228	0.570	...
Oat straw, sample 1	0.195	0.487	0.230

[1] THIS JOURNAL, 24, 142.

[2] Wolff's Aschen Analysen.

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TABLE I (*Continued.*)

Material.	Sulfur. Per cent.	Sulfur trioxide. Per cent.	Sulfur trioxide in ash.[1] Per cent.
Oat straw, sample 2	0.218	0.545	...
Onions	0.568	1.419	0.300
Potatoes	0.137	0.343	...
Rape tops	0.988	2.470	1.132
Rapeseed meal	0.456	1.140	0.381
Rice	0.126	0.315	0.003
Rice bran	0.181	0.452	0.022
Rutabagas, sample 1	0.817	2.041	...
Rutabagas, sample 2	0.632	1.579	...
Rye	0.123	0.309	...
Rye straw	0.049	0.123	...
Soy bean	0.341	0.852	0.085
Sugar beet, late field sample	0.128	0.320	0.160
Sugar beet, stored roots	0.089	0.222	...
Sugar beet, early field sample	0.069	0.172	...
Sugar beet tops	0.433	1.082	0.790
Timothy	0.190	0.475	0.195
Turnips	0.740	1.849	0.897
Turnip tops	0.900	2.249	1.095
Wheat sample 1	0.170	0.425	0.007
Wheat sample 2	0.164	0.410	...
Wheat sample 3	0.176	0.440	...
Wheat bran, sample 1	0.200	0.499	0.005
Wheat bran, sample 2	0.224	0.559	...
Wheat gluten	0.860	2.149	0.011
Wheat straw, sample 1	0.119	0.297	0.132
Wheat straw, sample 2	0.160	0.399	...

Table I discloses some very interesting facts. The results are in harmony with those of other investigators in showing a much higher content of total sulfur trioxide in plant materials than is found in the ash. This is particularly true in the seeds where the sulfur exists largely in organic form in the protein molecule. There the loss by ignition is very large.

There is one hundred times as much sulfur trioxide in rice grain as in the ash of that grain and forty times as much in the corn grain as in its ash. In wheat the same condition is true, while in the oat, cottonseed and soy bean the total sulfur trioxide recovered in the grain by the fusion method is about ten times that found in the ash. In onions, cabbage and turnips the amounts found in the green tissue were from two to four times that recovered in the ash. These materials contain volatil sulfur oils which are in part responsible for the sulfur lost on ignition.

In the case of the hays and straws the losses of sulfur by ignition have not been so large as in the seeds and in those plants rich in sulfur oils. Presumably a considerable part of the sulfur exists in plant stems as sulfates and consequently is permanent on ignition. In mixed hay, for

[1] Wolff's Aschen Analysen.

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example, the amount of sulfur trioxide recovered in the ash is nearly as large as that found in the original material, but in alfalfa and clover hay the recovery amounts to about 50 per cent. Of course the probable variation in the total sulfur content of different samples of material must be taken into consideration. This would apply especially to such parts of the plant as the stem and leaf, but not in the same degree to the seed.

Amounts of Sulfur Trioxide Removed by Crops.

The very important fact which the above data furnishes is that farm crops remove much more sulfur from the soil than has been supposed. Based on Wolff's ash analysis a 100-bushel corn crop per acre (grain only) would remove about one-half pound of sulfur trioxide, while the actual total sulfur trioxide removed, according to our analysis, would be over 20 pounds. For the purpose of clearly showing what amounts of sulfur trioxide are removed by average farm crops Table II has been constructed. The average figures used for these crops are quoted, in part, from a table constructed by Warington.[1]

TABLE II.—POUNDS OF SULFUR TRIOXIDE AND PHOSPHORUS PENTOXIDE REMOVED PER ACRE BY AVERAGE CROPS.

Crop.	Dry weight Pounds.	From Wolff's ash analyses, sulfur trioxide Pounds	Actual sulfur trioxide Pounds.	Phosphorus. pentoxide. Pounds.
Wheat grain, 30 bushels	1530	0.15	6.4	14.2
Wheat straw	2653	3.40	9.3	6.9
Total crop	4183	3.55	15.7	21.1
Barley grain, 40 bushels	1747	1.0	6.6	16.0
Barley straw	2080	4.1	7.7	4.7
Total crop	3827	5.1	14.3	20.7
Oat grain, 45 bushels	1625	0.8	7.5	13.0
Oat straw	2353	5.4	12.2	6.4
Total crop	3978	6.2	19.7	19.4
Corn grain, 30 bushels	1500	0.15	6.4	10.0
Corn stalk	1877	5.20	5.6	8.0
Total crop	3377	5.35	12.0	18.0
Meadow hay	2822	9.8	11.3	12.3
Red clover hay	3763	8.2	15.4	24.9
Alfalfa hay	9000	37.8	64.8	39.9
Bean grain, 30 bushels	1613	...	9.4	22.8
Bean straw	1848	...	4.9	6.3
Total crop	3461	...	14.3	29.1

[1] "Chemistry of the Farm, 9th Edition", p. 64.

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TABLE II (*Continued*).

Crop.	Dry weight. Pounds.	From Wolff's ash analyses, sulfur trioxide. Pounds.	Actual sulfur trioxide. Pounds.	Phosphorus pentoxide. Pounds.
Turnip root	3126	27.8	57.8	22.4
Turnip leaf	1531	16.6	34.4	10.7
Total crop	4657	44.4	92.2	33.1
Sugar beet root	4320	6.9	9.5	20.2
Sugar beet leaf	1848	14.5	20.0	13.1
Total crop	6168	21.4	29.5	33.3
Potatoes	3360	...	11.5	21.5
Tobacco leaf	1800	...	16.0	8.0
Tobacco stalk	3200	...	5.0	8.0
Total crop	5000	...	21.0	16.0
Cabbage	4800	62.8	98.0	61.0

For purposes of comparison, the amounts removed as calculated from Wolff's ash analyses are given in a number of cases. In addition to the above figures there are also included the amounts of phosphorus pentoxide removed by average crops. This is done for the purpose of comparing the amounts of these two very essential constituents removed by plant growth. It will also serve as a basis for the proper treatment of the question of sulfur fertilization.

A study of Table II reveals the fact that the average crop of seed from the cereal plants removes from the soil about half as much sulfur trioxide as phosphorus pentoxide and that the straws remove a somewhat larger quantity. The hays are not widely different in the proportion of these important ingredients removed, although alfalfa removes annually about twice as much sulfur trioxide as phosphorus pentoxide. The Cruciferae are heavy sulfur-using plants and the total sulfur trioxide removed by these is large. An average acre crop of turnips or cabbage appropriates nearly 100 pounds of this compound.

Amounts of Sulfur Trioxide in Soils.

No one questions the absolute necessity of sulfur for plant growth. It is necessary for the production of plant proteins and all the plant proteins that have been investigated contain sulfur. Only one class of proteins is known to be free from sulfur and that is the class of protamines of animal origin which, however, have not as yet been isolated from plant tissue.

The imperative necessity of maintaining an ample supply of this element for plant production is as important as maintaining a supply of phosphorus, nitrogen or any of the other elements essential for plant

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development. The apparent reason why so little attention has been given to this element in the schemes of fertilization for permanent plant production has been due to the fact that it was believed that crops removed but little from the soil and consequently the supply was ample for continuous production.

Bogdanov[1] in 1899 called attention to the practical importance of sulfur in agriculture and believed that it should be applied occasionally as a sulfate for the express purpose of maintaining in the soil an adequate supply of this element. Dymond, Hughes and Dupe[2] have also touched upon this subject and concluded that there was not sufficient sulfur in the soil for the greatest yield of crops rich in protein, but that for *cereal crops* and permanent pasture the soil and rain would provide a sufficient quantity. So far as we can find in the literature no further treatment of the subject has been made.

Investigation of the forms of sulfur in soils has been made by Berthelot and Andre.[3] According to these investigators sulfur exists in soil as (1) sulfates and sulfides; (2) ethereal sulfur; (3) in organic compounds. Very probably the chief forms in all normal soils will be those existing as sulfates and those in the organic matter of the soil. Sulfides would rarely exist except in water-logged soils where reducing processes are prominent. Ethereal sulfates would probably be found only after fertilization with the urin of animals, and then only in small amounts.

There are some difficulties in the estimation of the total sulfur of soils. Fusion of the soil with an alkali is somewhat tedious, although probably the most accurate procedure. The large amount of silicates and their incomplete removal before final precipitation with barium chloride may endanger the absolute accuracy of the method. Extraction in the wet way with strong oxidizing agents, while probably not absolute, will, nevertheless, give the amount of sulfur that can reasonably be expected to become available to the crop in future years. Van Bemmelen[4] compared several methods for the estimation of sulfur in soils, obtaining the highest results by extraction with aqua regia. Trials by the method of ignition with sodium carbonate and potassium nitrate and the method of ignition in a stream of oxygen as used by Berthelot gave him slightly lower results than with aqua regia. It is safe to assume that digestion and extraction with a strong oxidizing agent will remove all sulfates, oxidize sulfides to sulfates, and split up any ethereal sulfates present to form sulfuric acid, and at least partly oxidize the sulfur existing in organic forms. It probably will not give the total sulfur present in the organic material of the soil.

[1] Abstract, *Expt. Sta. Record*, 11, 723.
[2] *J. Agr. Sci.*, Vol. 1 (1905).
[3] *Ann. chim. phys.*, 25, 305 (1892).
[4] *Landw. Versuch. Sta.*, 37, 284 (1890).

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Most of the determinations of sulfur in soils carried out heretofore have been made by extraction with strong hydrochloric acid. This has been done either by the long-time extraction method as recommended by Hilgard or by the method adopted by the Association of Official Agricultural Chemists. These methods will presumably give all sulfates and ethereal sulfur, but not that existing as sulfides, or the sulfur in combination with the organic matter of the soil. Hilgard found from his analyses of many types of soil that the average amount of sulfur trioxide in sandy soils was 0.055 per cent. while in the clay soils examined it amounted to 0.075 per cent. This, on the basis of an acre foot of three million pounds, would amount in the first instance to 1650 pounds, and in the latter case to 2250 pounds. The average amount of phosphorus pentoxide as given by Hilgard for the same sandy soils was 0.087 per cent. and 0.141 per cent. for the clay soils. On the same basis of calculation an acre foot would contain in the first case 2610 pounds and in the second 4230 pounds of phosphorus pentoxide. Whitson and Stoddart[1] also have shown that the average phosphorus pentoxide content of the surface eight inches of many Wisconsin soils is about 2940 pounds.

These figures are introduced for the purpose of showing that the amount of sulfur in all normal soils is comparatively low.

Effect of Continuous Cropping on the Sulfur Content of the Soil.

To determin definitly the effect of continuous cropping on the sulfur content of soils, a number of analyses of both cropped, virgin and manured soils have been made. Two methods were used for the determination of sulfur trioxide.

The first was a slight modification of the Van Bemmelen method. That investigator used aqua regia for the extraction, while in our method nitric acid and bromine were used.

The second method consisted of fusion with sodium peroxide, and as it gave more accurate results will be described in detail. Ten grams of soil were placed in a 100 cc. nickel crucible, moistened with water, about 10 grams of a weighed 20-gram portion of sodium peroxide added, and the mixture thoroughly stirred with a platinum rod. The crucible was placed over an alcohol flame and heated moderately until the mass was dry. The remainder of the sodium peroxide was then added, the cover placed on the crucible, strong heat applied until the mass melted, and kept in this condition for 10 minutes. It was then allowed to stand over a lower flame for 1 hour. The crucible was removed, cooled, placed in a 600 cc. casserole, hot water added and the fused mass removed. It was neutralized with hydrochloric acid and then further acidified with 10 cc. of hydrochloric acid. The volume was made up to about 450 cc. and boiled for 15 minutes, or until no undecomposed portion of the fused

[1] *Research Bulletin*, 2, 1909, Wisconsin Expt. Station.

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mass remained on the bottom. The covered casserole was allowed to stand on the steam bath over night, filtered through a "nutsche" and the residue thoroughly washed with successive small portions of hot water. The filtrate and washings, if over 500 cc., were evaporated below that volume, refiltered and the volume made up to 500 cc. Aliquot portions of 250 cc. each were heated to boiling, barium chloride added, boiled for 5 minutes and set aside on a steam bath for 24 hours. The volume was not allowed to decrease, as silicic acid may be precipitated out if much evaporation takes place. After standing for this length of time the barium sulfate was filtered off, washed, ignited and weighed. In the determinations made by this method the precipitate was free from silica as demonstrated by the hydrofluoric acid test.

Both these methods were compared with the method of the Official Agricultural Chemists with the following results: The soil used was from the surface 8 inches of one of the experimental plots at the University Hill Farm.

	Per cent. of SO_3.
Official method	0.019
Fusion method	0.043
Nitric acid bromine method	0.037

Since the official method gave lower results than either the fusion or wet extraction method it was not used for our work. Instead, for the purpose of greater completeness, all the soils investigated were subjected to both the fusion and nitric acid bromine methods. There was close agreement between the results secured by the two methods, but with a uniform tendency for the fusion method to give slightly higher results. This is to be expected as that method should include the total sulfur of the soil, while by the wet method some of the organic sulfur may escape complete oxidation. In the analyses reported only those results secured by the fusion method are recorded.

Sulfur Trioxide in Soil Samples.

Ten different soils from several parts of this state were first investigated. They were both virgin and (the same soils) cropped but generally unmanured. The determinations of sulfur trioxide were made on pairs of samples, one from the cropped field and the other from the adjacent virgin soil. In each case the surface 8 inches were taken and every precaution to secure virgin soils of drainage and topography similar to that of the cropped soil was observed. Analyses are also given in the later part of this article of virgin soils and the same soils heavily manured, but in two instances continuously cropped to such heavy sulfur-using plants as the cabbage.

The following is a brief history of the *unmanured* samples:

No. 1 (cropped). "Janesville. Cropped 63 years. During the first

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34 years wheat was grown almost continuously. Since 1878 it has been rotated to corn, barley, oats and rye. It has never been seeded down or manured and is in a badly exhausted condition."

No. 2 (cropped). "Edgerton. Cropped about 60 years, largely to wheat at first, but during the last 40 years it has been farmed in a rotation, consisting of two crops of corn, one of oats and two of clover and timothy of which the first was cut and the second pastured. The field has not produced good crops during the last 10 years. It has been manured but once."

No. 3 (cropped). "Milton Jct. Cropped 52 years, chiefly to wheat during the first 15 years, since then it has been rotated to oats and barley with a few years of timothy. It has been manured 10 times with an average of 10 loads per acre each time. The field does not now produce good crops."

No. 4 (cropped). "Milton Jct. Cropped 50 years. Rotated to corn and oats for about 40 years, then grew one crop of barley, one of corn, one of beets and now in alfalfa. Alfalfa doing poorly. Soil acid. Manured once."

No. 5 (cropped). "Evansville. Cropped 60 years, early years chiefly wheat. History for last 28 years—10 years timothy and clover; 12 crops of corn; 6 crops of oats. Manured three times. Manure usually sold."

Table III gives the results of the analyses of the virgin and cropped soils; the loss of sulfur trioxide by cropping as determined from the analyses; the estimated amount of sulfur trioxide removed by the crops; the amount added in the manure; and the amount removed by the crop in excess of that added in the manure. It is estimated that the average amount of sulfur trioxide removed every year by corn, the small grains, clover and timothy was 12 pounds. This amount is somewhat below the figure given in Table II for average crops, but the smaller amount is taken because of the falling off of crop yields in the later years of the field's history. The average amount of sulfur trioxide added in the manure was estimated on the basis of several analyses, at two pounds per ton of manure with an application of 10 tons yearly.

Table III indicates that on the average about 40 per cent. of the sulfur trioxide has been lost from the cropped soils. In every case there is a lower percentage of sulfur trioxide in the cropped soil than in the virgin soil. The estimated amount removed by the crops, minus that supplied in the manure, is in two cases in excess of that indicated to have been lost by the analysis. Such discrepancies are due, possibly, to variations in the soil itself, inaccurate estimates of the amounts of crop removed, and the influence of the influx of sulfates with the upward movement of soil water. On the other hand the estimated average amounts of sulfur

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trioxide removed by the crops and that indicated by the analyses, are almost identical. This estimate on the soil is based on the surface 8 inches and the weight of two million pounds per acre. Little importance, however, should be attached to these estimated amounts removed, as there must still be losses of sulfur trioxide due to drainage, which the figures do not include. The important thing that the table teaches is that continuous cropping without adequate fertilization shows a large decrease in the sulfur trioxide content of the soils examined.

TABLE III.—INFLUENCE OF EXHAUSTIVE CROPPING ON THE SULFUR TRIOXIDE CONTENT OF SOILS.

Soil sample. No.	SO_3 in virgin soil. Per cent.	SO_3 in cropped soil. Per cent.	Amount per acre (estimated). Loss by cropping according to analyses. Pounds.	Removed by crops. Pounds.	Added in manure. Pounds.	Removed by crop in excess of that added in manure. Pounds.
1.....	0.107	0.066	820	756	...	756
2.....	0.101	0.058	860	720	20	700
3.....	0.033	0.019	280	624	200	424
4.....	0.127	0.088	780	600	20	580
5.....	0.055	0.032	460	720	60	660
Average,	0.084	0.052	640	684	60	624

Effect of Liberal Manuring on the Sulfur Trioxide Content of Soils.

In order to determin what would be the effect of liberal manuring with farm manure on the sulfur trioxide content of soils, several samples of known history were subjected to an examination. The corresponding virgin soils were also examined. The history of the cropped samples is as follows:

No. 6 Evansville. Cropped 60 years. Wheat up to 1860. Since 1860 general rotation of two years in corn, one to two years in meadow, and one year in pasture. Manured every year while in corn at the rate of 10 loads to the acre. Crop yields good.

No. 7 Berryville. Continuously in cabbage until the crop failed some 10 years ago. Manured heavily with stable manure until three years ago. The last three years fertilized annually with 1400 pounds per acre of Homestead fertilizer. Surface two inches rejected in taking samples.

No. 8 Kenosha. Past 15 years in cabbage, alternating every year with corn or potatoes. Chicago stable manure freely applied with yearly applications of about 10 loads. None used in 1909.

The results are given in Table IV.

The results show that the sulfur content of these soils was maintained and even slightly increased by the liberal application of farm manure.

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TABLE IV.—INFLUENCE OF LIBERAL MANURING WITH FARM MANURE ON THE SULFUR TRIOXIDE CONTENT OF SOILS.

Soil sample. No.	SO_3 in virgin soil. Per cent.	SO_3 in cropped and manured soil. Per cent.
6	0.061	0.075
7	0.108	0.115
8	0.119	0.140
Average	0.096	0.110

Other Factors in the Gain and Loss of Sulfur Trioxide from Soils.

In addition to the sulfur added to the soil with applications of farm manure or certain commercial fertilizers there is also a small amount brought to the land by rain water. This sulfur in the atmosphere has its origin almost wholly in the burning of fuel, especially soft coal. The amount of sulfur trioxide brought to an acre surface yearly has been determined at Rothamsted, England. Warington[1] gives the amount as about 17 pounds and adds further that sulfates in rains "will, to a considerable extent, meet the demands of most cultivated crops."

Later determinations made at Rothamsted and furnished us by Director Hall show an average annual precipitation per acre of about $18^1/_2$ pounds of sulfur trioxide.

In England large amounts of soft coal are burned and it was believed not improbable that the amount brought to a surface acre annually by the rain in the open country of our northern states, especially where soft coal is used to but a limited extent, would not be as large as the amount found in England. For the purpose of collecting data on this point a rain gage with a collecting surface equal to one square foot was set up at the University Hill Farm located three miles west of the city of Madison, Wisconsin. It was placed in an open field and at least a mile from any chimney using considerable quantities of coal. The rain water was collected in a copper bottle, containing a trace of sodium bicarbonate in order to fix any sulfurous acid. A fine wire screen was placed above the funnel of the gage for the purpose of excluding any material accidentally blown or falling into the gage.

The samples of water collected were analyzed for total sulfur at the end of each month. The results are given in Table V and reported as pounds per acre of sulfur trioxide; the monthly rainfall at the time the analyses were made is also recorded.

Not enough data are at hand to warrant establishing an average annual figure, but until such data are accumulated the tentative statement can be made that the amount of sulfur trioxide brought yearly by rain to an acre surface of land at this location will probably not be less than that

[1] "Chemistry of the Farm," p. 19, 9th edition.

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found at Rothamsted, England, which is 17–18 pounds. The total amount brought down in the five months recorded was 10.70 pounds with a rainfall of 11.14 inches.

TABLE V.—AMOUNTS IN POUNDS OF SULFUR TRIOXIDE BROUGHT TO THE SURFACE ACRE MONTHLY.

Month.	SO_3 Pounds.	Rainfall. Inches.
June, 1910	2.36	1.31
July, 1910	0.60	0.81
August, 1910	4.47	6.56
September, 1910	2.66	1.83
October, 1910	0.61	0.63
Total	10.70	11.14

Losses of Sulfur Trioxide from Soils by Drainage.

While the atmosphere can serve as a considerable source of sulfur trioxide to the soil, nevertheless as a compensating factor, it is probably more than offset by the losses that soils sustain by drainage. It is well known that most river and lake waters, which in part represent the drainage waters from our soils, contain considerable quantities of sulfates. These have been dissolved out of the soil. The Rothamsted Experiment Station gives some definit data on the losses of sulfur trioxide in the drainage water from soils. The drainage waters from the wheat plots of Broadbalk field have been collected from time to time and completely analyzed by Voelcher and Frankland. From the unmanured plots they report the quantity of sulfur trioxide in the drainage water at 24.7 parts per million, while the quantity varied from 41.0–106.1 parts per million in the waters from the plots receiving various fertilizer treatments.

Assuming, as Hall does[1] in his discussion of losses by drainage from these plots, a mean annual drainage equal to 10 inches of water, the unmanured plots would lose approximately 50 pounds of sulfur trioxide annually per acre, while those receiving fertilizers containing varying amounts of sulfates would lose from 85–220 pounds annually per acre. It will be seen from the above data that the loss of sulfur trioxide by drainage is considerable and in the case of the unmanured plots it is nearly treble the amount brought by rain to an acre surface from the atmosphere. While these figures may not be applicable to all climates and all soils, nevertheless it would be conservative to state that the loss by drainage at least equals and probably exceeds the amount brought to the soil from the atmosphere in the humid regions of America.

General Discussion.

The general question raised by the data presented above is one of great importance. The fact that common crops remove from the soil con-

[1] "The Soil," p. 200.

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siderable quantities of the element sulfur, while the compensating factor of supply from the atmosphere is very probably offset by the losses which the land sustains by drainage, makes it apparent that for the maintenance of a permanent supply of sulfur in the soil, this element must be added systematically either as a constituent of commercial fertilizers, or with the farm manure.

The supply of sulfur in soils is low, the surface eight inches of a normal soil containing sulfur trioxide sufficient for about 100 crops of barley, and this would suppose that the crop could produce normal yields with a steadily decreasing supply of sulfur. The upward movement of water within the soil occasioned by surface evaporation would possibly aid in bringing sulfates from the lower soil areas, but this could not continue indefinitly. The sulfur trioxide content of subsoils according to the analyses made by Hilgard is no greater than that of the surface soil.

Many factors are operative in the maximum production of crops; ample supplies of essential elements, proper biological agents, absence of toxic substances, and proper physical environment are all important soil factors. So many factors are operative that an optimum condition is probably seldom obtained. For this reason the disturbance of the equilibrium in the soil by the addition of a single agent is often followed by better crop production. Whether it affects the biological agents, improves the sanitary conditions, alters the physical status of the soil, or acts by furnishing an ample supply of the elements essential for plant growth is always difficult to answer, but that there must be maintained an ample supply of the essential elements, is one of the first principles of plant production.

Most normal soils contain an abundance of the essential elements, potassium, iron, magnesium and calcium. Nitrogen, phosphorus and sulfur alone are of a low percentage. The former two are to-day recognized as valuable essentials of commercial fertilizers, and field experiments in many instances have shown the utility of the application of potash salts in available form. When calcium is added it is usually as a carbonate and more for the purpose of maintaining a neutral or slightly alkaline reaction in the soil solution than as a source of calcium for plant growth.

The use of sulfates in fertilizers has been unconsciously practiced for many years. The acid phosphate of the fertilizer industry is a product containing a large proportion of calcium sulfate. Whether the beneficial results accruing from its application are to be attributed alone to the phosphorus it supplies or whether they are twofold and due to both the phosphorus and sulfur contained in this material are questions raised by this investigation. It is not impossible that the superior results sometimes obtained in field practice with acid phosphates over other phosphates, such as Thomas slag, or ground rock phosphate, are not due entirely to

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differences in solubilities, but to the additional sulfur supplied by the former material. The superior results so often noted from the use of potash salts when furnished as sulfates rather than chlorides may rest in part upon the sulfur content of the material added.

It was once common practice to use gypsum as a fertilizer. The beneficial effects often resulting from the use of this material have been explained on the basis of its action as a stimulant. Boussingault showed that its application increased the amount of potassium taken up by the plant. This was accomplished through a double decomposition of potassium silicates with liberation of potassium sulfate. Consequently its action was said to be indirect and it was classed as a stimulant for the reason that while it often produced increased plant growth, it furnished no necessary plant elements. While the above reaction may be entirely true, the explanation appears to be only partial. If the idea here presented, that sulfur may become a limiting element in crop production, is true, then the beneficial result accruing from the use of gypsum may result in part from its sulfur content.

In the 25 years of carefully recorded plot fertilization experiments by the Pennsylvania Experiment Station,[1] the evidence for the necessity of occasional sulfur applications is negative. While these experiments were not planned to answer the question of sulfur requirements, nevertheless they are the only experiments available so far as the authors are aware, which shed any light at all on the question involved. In plots 9 and 17 the treatment consisted of dried blood, muriate of potash and dissolved boneblack, which contained calcium sulfate sufficient to furnish probably from 30–40 pounds of sulfur trioxide per acre. On plots 12 and 35 the treatment was dried blood, muriate of potash and ground bone. Identical quantities of phosphorus pentoxide and potassium oxide were added in the two treatments, with 24 pounds of nitrogen in the first mixture and 30 pounds in the latter.

Unless the muriate of potash and dried blood used contained sulfates sufficient[2] for all crop needs, then the only difference in the kinds of essential elements added was in the greater amount of sulfur contained in the first mixture; yet the total annual yield in crops over a period of 25 years was slightly in favor of the second treatment. Nevertheless, while an annual removal of 15 pounds of sulfur trioxide per acre by the crops grown in the above experiment may not as a single factor be sufficient to reduce the productivity of the soil receiving sufficient nitrogen, phosphorus and potassium in 25 years, it appears probable that this could

[1] "Report of Penn. State College," 1907–1908, p. 80.

[2] From some of our own analyses of dried blood and muriate of potash the amounts of these materials used in the Pennsylvania experiments could have furnished about 14 pounds of sulfur trioxide per acre.

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not continue indefinitly. Our own data on the partial depletion of sulfur in soils unmanured but cropped for 50–60 years is evidence in support of this view.

Unfortunately none of the experimental plots at Rothamsted, England, have been deliberately planned with respect to the effect on long-continued cropping, of fertilizers with and without applications of sulfur.

Careful experimentation and practical agriculture must decide in what form sulfur, when needed, should be added to the soil. Economy and safety are the factors involved. The principal sulfates normal to the soil are those of calcium, magnesium, and potassium. No harm can result from a judicious use of any of these. Sulfur can be added to the soil either as land plaster; with acid phosphate, in which it exists as calcium sulfate; or as a sulfate of potassium or ammonium. All these materials are now offered by the trade.

Conclusions.

1. The sulfur content of a number of our common farm products has been determined and in agreement with other investigations the quantity is much larger than found by Wolff in the ash from such products.

2. The amount of sulfur trioxide removed by crops is considerable, being equal in the case of average crops of cereal grains and straws to about two-thirds of the phosphorus pentoxide removed by these crops; the grasses of mixed meadow hay remove quite as much sulfur as phosphorus, while the legume hays may approach, and in the case of alfalfa, even exceed in this respect. Members of the Cruciferae, as the cabbage and turnip, are heavy sulfur-using crops and may remove two to three times as much sulfur trioxide as phosphorus pentoxide. An average acre crop of cabbage will remove about 100 pounds of sulfur trioxide.

3. Normal soils are relatively poor in total sulfur trioxide, a limited number of analyses showed a percentage content of from 0.033–0.140; most of them contained less than 0.10. An acre foot will contain from 1000–3000 pounds of total sulfur trioxide. About the same quantity of phosphorus pentoxide will be found in an acre foot of normal soil. These results for sulfur trioxide are based on analyses made by the method of fusion with sodium peroxide. Determinations by extracting with hydrochloric acid or with nitric acid and bromine will not give the total sulfur content of soils.

4. Soils cropped for 50–60 years and either unmanured or receiving but slight applications during that period have lost on the average 40 per cent. of the sulfur trioxide originally present as determined by comparison with virgin soils.

5. Where farm manure has been applied in regular and fairly liberal quantities the sulfur content of the soil has been maintained and even increased.

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6. The total sulfur trioxide precipitated at Madison, Wis., with the rain amounted in the five months of June to October, 1910, inclusive, to 11.7 pounds per acre. The annual amount may tentatively be placed at 15–20 pounds.

7. The losses of sulfur trioxide by drainage, based on the analysis of the drainage waters at Rothamsted, England, and on a yearly drainage of 10 inches, would amount to about 50 pounds per acre yearly.

8. Even with much less loss by drainage it does not appear that the atmosphere can serve as a complete compensating factor for losses of sulfur trioxide which soils sustain through both cropping and drainage. The partial depletion of the sulfur of the soil by continued cropping without fertilization is evidence in support of this view.

9. From the data here presented it appears that for permanent and increased production of farm crops such systems of fertilization must be inaugurated as will supply to the soil from time to time, in addition to the elements now recognized as necessary, a sufficient quantity of sulfur to meet the losses sustained by cropping and drainage.

10. Such sources of sulfur are farm manures; the trade fertilizers, such as superphosphate, ammonium sulfate and sulfate of potassium; and the so-cal[illegible]oil stimulant, gypsum or calcium sulfate.

No attention. so far as we are aware, has been directed to this problem in America. It is hoped that the thesis here presented may be made the subject for further research by chemists and agronomists and the relative importance and necessity for sulfur in systems of fertilization finally established.

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TWO COMPOUNDS ISOLATED FROM PEAT SOILS.

BY CHAS. S. ROBINSON.

Received February 11, 1911.

Although the organic nitrogenous compounds in peat have been under investigation for over a hundred years the actual isolation of such compounds in the crystallin form had been attained only very recently. Suzuki,[1] by means of Fischer's esterification method, succeeded in isolating several of the mono- and di-aminoacids from a natural humic acid. Previous to this, Shorey[2] had isolated picolinecarboxylic acid from a soil containing 12.47 per cent. humus and Schreiner and Shorey[3] have since isolated this compound from several other soils. They have also isolated several diamino acids, purine bases and pyrimidine derivatives.[4] In all cases they extracted the soil with dilute alkali.

[1] *Bull. Coll. Agric. Tokyo*, 7, 513; abst. in *Chem. Zentr.*, 1907, II, 1.
[2] *Rept. Agr. Exp. Sta. Hawaii*, 1906, 37.
[3] U. S. Dept. of Agr., Bur. of Soils, *Bull.* 53.
[4] *Ibid.*, *Bull.* 74.

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Isolation of Leucine and Isoleucine from Peat.

The peat used for this purpose was a brown peat of a type common to this country. After drying at 110° it contained 2.53 per cent. nitrogen of which 9.18 per cent. was in the amido form. This was determined by heating with sulphuric acid, filtering and distilling off the ammonia after making the liquid alkaline with magnesium oxide. In the air-dried state it contained 11.18 per cent. moisture and 16.00 per cent. ash. It was ground in a mill so that practically all of it would pass through an 80-mesh sieve.

The nitrogenous material was extracted by heating it for forty-eight hours on the sand bath with 25 parts by weight of 25 per cent. sulphuric acid in a flask fitted with a reflux condenser. While still hot, the dark brown liquid was filtered, with suction, through a Buchner funnel having a solid unglazed, porcelain bottom. The insoluble material was returned to the flask, heated with a fresh supply of water and again filtered. This was repeated several times until the wash water came through colorless. The filtrate and washings were made alkaline with slaked lime and the precipitate of calcium sulfate allowed to settle. The supernatant liquid was then poured through a filter and the precipitate washed several times by decantation with hot water. The liquid thus obtained was concentrated to about one-third its volume and filtered from a small precipitate of calcium sulfate and humus. Barium hydroxide was added to the filtrate in slight excess and the precipitate of barium sulfate filtered off and thoroughly washed.[1] The hydroxides of barium and calcium remaining in solution were then removed by passing carbon dioxide into the hot solution and filtering off the precipitated carbonates by suction. By this process all of the sulfuric acid can be removed together with the reagents used for its removal, leaving only the products of the extraction in solution. Most of the brown, amorphous, humus material is held back so that at the end one has, at most, only a light brown solution. The amount of mineral matter was very small and was precipitated as a light-colored, sandy powder, during the concentration, before the organic matter came down. After removing this small precipitate, the solution was made slightly acid and a solution of phosphotungstic acid slowly added until it failed to cause a further precipitation. The precipitate thus formed was light gray and flocculent. It was filtered off and washed with hot water. Both the filtrate and precipitate were then boiled with an excess of barium hydroxide and filtered, after which the excess of barium hydroxide was removed with carbon dioxide and the

[1] Where only small quantities of peat and sulphuric acid are used, it is, of course, better to precipitate all of the acid with barium hydroxide. When large quantities of acid are being used, however, it is more economical to precipitate the bulk of it with lime and use the barium only for that which remains in solution as calcium sulfate.

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solutions concentrated. The one resulting from the decomposition of the phosphotungstic acid precipitate yielded only a brown, viscous mass, which failed to crystallize.

A light yellow scale formed on the surface of the other solution and as the concentration was continued, waxy knobs and clusters were formed on the sides of the dish. This material was separated from the rather oily mother liquor, dissolved in water and, after boiling with animal charcoal, recrystallized. After several recrystallizations it was obtained colorless, separating in waxy knobs and clusters when allowed to crystallize slowly or as a white crust when the mother liquor was more concentrated. It was further purified by precipitation from a concentrated aqueous solution with absolute alcohol. After being purified in this way it crystallized in white flakes. It was readily soluble in water but almost insoluble in absolute alcohol and most organic solvents. The aqueous solution was neutral to litmus. When the solid substance was heated in a capillary tube it softened at 230° and decomposed at 265–269°, giving a white crystallin sublimate in the upper part of the tube. The mother substance analyzed as follows:

0.0696 g. subst. gave 6.7 cc. N at 25° and 748 mm.

Calculated for $C_6H_{13}O_2N$: N, 10.68. Found, 10.56 per cent.

Copper Salt.—Several hundred milligrams were dissolved in boiling water and the solution saturated with copper carbonate. Carbon dioxide was evolved and the solution turned dark blue. A light blue scum formed on the surface. The solution was filtered hot and concentrated, upon which a dark blue crystallin copper compound separated out. It gave 19.63 per cent. copper; calculated for $(C_6H_{12}NO_2)_2Cu$, 19.64 per cent.

These figures indicated that it might be one of the aminocaproic acids of which leucine is the most prominent. The light blue scum which had been filtered off was dissolved in water, in which it was difficultly soluble. From this it was evident that the original material contained two compounds, one forming a copper salt easily soluble in water, the other forming a copper salt difficultly soluble in this solvent. As was shown by Ehrlich, such is the case with leucine and isoleucine. His method for separating these two substances was based on the fact that the isoleucine copper salt is readily soluble in cold concentrated methyl alcohol while the corresponding leucine compound is practically insoluble. Unfortunately this ideal condition of affairs does not hold absolutely when both substances are present. In a mixture of these compounds some of the leucine copper salt dissolves in the alcoholic solution of the isoleucine salt while some of the latter is held back in the crystals of the former. For complete purification of the leucine, Ehrlich[1] suggested that, after extracting as thoroughly as possible, the leucine

[1] *Ber.*, 37, 1809 (1904).

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copper salt be decomposed with hydrogen sulfide, the copper sulfide be filtered off and the copper salt again formed and extracted as before. Several repetitions of this procedure should remove all of the isoleucine. Recrystallization from water removes the leucine completely from the isoleucine.

Leucine.—The solution of the mixed copper salts as originally obtained was taken to dryness on the steam bath. The resulting light blue, crystallin mass was extracted with small portions of cold concentrated methyl alcohol until the solvent was no longer colored after having been shaken some time with the salt. The solid residue was then dissolved in water and decomposed with hydrogen sulfide. After filtering off the copper sulfide the solution was saturated with copper carbonate, the excess filtered off and the solution taken to dryness as before. This copper salt was again extracted with methyl alcohol and the process repeated twice. The last extraction removed only a trace of copper from the solid residue. This was then dissolved in water, and decomposed with hydrogen sulfide. The copper sulfide was filtered off and the solution concentrated. It was levorotatory. The white crystallin substance which separated out gave the following rotation in 20 per cent. hydrochloric acid.

0.0455 gram substance in 11.1373 gram solution (0.4085 per cent.; 1.086 sp. gr.) gave +0.40° (Ventzke) rot. in a 2 dm. tube at 20°, sodium light.

$[\alpha]_D^{20}$ found = +15.62.
$[\alpha]_D^{20}$ *l*-leucine = +17.3.

When heated quickly in a capillary tube it melted at 287°. The copper salt gave the following figures for nitrogen and copper:

0.0585 gram substance gave 5.0 cc. moist nitrogen (28°, 738 mm.).

0.0291 gram substance gave 0.0072 gram CuO.

Calculated for $(C_6H_{12}O_2N)_2Cu$: N, 8.65; Cu, 19.64. Found: N, 9.10; Cu, 19.76 per cent.

Isoleucine.—The combined methyl alcohol extracts from the leucine were concentrated. After drying at 110°, the dark blue copper compound analyzed as follows: 0.0539 gram substance gave 0.0133 gram CuO.

Calculated for $(C_6H_{13}O_2N)_2Cu$: Cu, 19.64. Found, 19.72 per cent.

After recrystallizing once from water, the copper was precipitated by hydrogen sulfide and the solution concentrated. The pure, white crystallin compound was filtered from the mother liquor, washed with alcohol and ether and dried at 110°. It melted at 272° when heated quickly. It had the following specific rotation:

In water, 0.3227 gram substance in 14.6053 grams solution (2.21 per cent.; 1.0053 sp. gr.) gave +1.1° (Ventzke) rotation in a 2 dm. tube at 20°, sodium light.

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$[\alpha]_D^{20}$ found = +8.58.
$[\alpha]_D^{20}$ for isoleucine = +9.74.

In 20 per cent. hydrochloric acid, 0.1965 gram substance in 13.4543 grams solution (1.46 per cent.; 1.0871 sp. gr.) gave +3.25° (Ventzke) rotation in a 2 dcm. tube at 20°, sodium light.

$[\alpha]_D^{20°}$ found = +35.47.
$[\alpha]_D^{20°}$ isoleucine = +36.80.

It analyzed as follows for nitrogen:

Calculated for $C_6H_{13}O_2N$: N, 10.68. Found: N, 10.89 per cent.

From these results there can be no doubt as to the identity of the two compounds in question. Both of them are well known decomposition products of protein and one of them, leucine, was among the compounds isolated by Suzuki from humic acid.

Compounds from Black Peat.

Compounds from Black Peat.—A sample of black peat described by Jodidi[1] was extracted with 25 per cent. sulfuric acid and the extract treated as above. Upon concentrating the sulfate-free liquid, the characteristic yellow scale formed. It was separated from the mother liquor and purified as in the previous case. The quantity was too small to permit of a separation of the isomers. The material was converted into the copper salt which analyzed as follows:

0.0720 gram substance gave 0.1169 gram CO_2 and 0.0485 gram H_2O.
0.0302 gram substance gave 0.0075 gram CuO.

Calculated for $(C_6H_{12}NO_2)_2Cu$: C, 44.48; H, 7.47; Cu, 19.64.
Found: C, 44.29; H, 7.53; Cu, 19.85.

The substance was evidently a mixture of the two compounds described above.

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FASTING STUDIES. III. NITROGEN PARTITION OF TWO MEN THROUGH SEVEN-DAY FASTS FOLLOWING THE PROLONGED INGESTION OF A LOW-PROTEIN DIET; SUPPLEMENTED BY COMPARATIVE DATA FROM THE SUBSEQUENT FEEDING PERIOD.

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Introduction.

The metabolism of fasting men has been studied by a number of investigators but accurate studies of the nitrogen partition during fasting, in

[1] Mich. Exp. Sta., *Technical Bull.* 4, 25.

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which the excretion of creatine and creatinine has been considered, are few in number and have all been made since the introduction of Folin's methods for the determination of these two substances. Benedict's[1] work in which he determined the nitrogen partition as well as the respiratory exchange and the metabolism of chlorine, sulfur and phosphorus is the most comprehensive work upon the metabolism of man during fasting. He also includes data upon the metabolism during the period of regeneration following the fast. Cathcart's[2] work upon Beauté deals with the nitrogen partition and the excretion of the inorganic substances. Data for a period of three days following the fast in which the subject received a nitrogen-free diet and a two-day period on an egg and milk diet are included. In an experiment in which the fasting woman Flora Tosca served as subject, van Hoogenhuyze and Verploegh[3] determined creatinine as well as total nitrogen, urea, uric acid, acidity, phosphates and chlorides. Brugsch and Hirsch,[4] Bonniger and Mohr,[5] and Baumstark and Mohr[6] determined the excretion of total nitrogen and amino acids, and the extent of putrefaction during the sixteen-day fast of a woman (Schenk).

Lehmann, Müller, Munk, Senator and Zuntz[7] report the results of experiments upon Cetti (10 days) and Breithaupt (6 days) in which careful studies were made of the respiratory exchange as well as of the alterations in the composition of the urine, feces and blood: body weight determinations were also made and other physical measurements ascertained. Brugsch[8] investigated the changes in the urinary nitrogen of Succi during a thirty-day fast and demonstrated a decrease in the urea output and an increase in the quantity of ammonia excreted. This latter increase he explained as due to acidosis. Diaber,[9] as the result of a twenty-day fast on Succi, records a decreasing body weight, chlorine excretion and urea output; also a pronounced increase in the excretion of urobilin. Ajello and Solaro[10] record results upon a twenty-one-day fast of Succi including the determinations of urea, acidity, phosphorus, chlorides, indican and blood changes. O. and E. Freund[11] report a twenty-one-day fast upon Succi in which they show a decrease in urea, creatinine (Neubauer) and total sulfur with an increased output of neutral sulfur. Urobilin was

[1] *Carnegie Publication No.* 77 (1907).
[2] *Biochem. Z.*, 6, 109 (1907).
[3] *Z. physiol. Chem.*, 46, 440 (1906).
[4] *Z. exper. Path. und Ther.*, 3, 638 (1906).
[5] *Ibid.*, 675.
[6] *Ibid.*, 687.
[7] *Virchow's Arch.*, 131, supplement (1893).
[8] *Z. exp. Path. Ther.*, 1, 419 (1905).
[9] *Schweiz. Woch. Chem. Pharm.*, 34, 395 (1896).
[10] *La Riforma medica Ann.*, 9, 542 (1893); from *Jahrb. Fortschr. Thier-Chem.*, 24, 544 (1894).
[11] *Wien. klin. Rundschau*, 15, 69 and 91 (1901).

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increased in amount from the first day of the fast and from the eighth day sugar was present in the urine. Luciani[1] reports a thirty-day fast of Succi, during the last nine days of which he received peptone, sugar, gelatin, etc. Johansson, Landergren, Sónden and Tigerstedt[2] report the five-day fast of a medical student in which results are given from the examination of the feces and urine as well as from a study of the respiratory exchange. Paton and Stockman[3] report a thirty-day fast upon Jacques in which the urea determinations were made by the hypobromite method.

Description.

Purpose and Plan.—The purpose of this experiment was to study the nitrogen partition of normal fasting men, when performing their customary duties; changes in body weight were also observed. The experiment was conducted upon two men and consisted of three periods, a fore period of four days during which they received a constant diet embracing a uniform water ingestion, a fasting period of seven days and an after-period of eight days.

Subjects.—The subjects of this experiment were two instructors E and H connected with the Chemistry Department of this University. Both subjects were somewhat taller than the average man and were of approximately equal height and build and of a more or less even temperament. Subject E was 23 years old, six feet in height and weighed 74 kilograms. Subject H was 23 years old, six feet one inch in height, and weighed 71 kilograms.

The men were favorably disposed toward fasting, having in previous years practiced it occasionally for intervals of from one to two days. They were at the time engaged in research and realized the importance of careful attention to detail and the strict obeyance of instructions.

The previous dietary history of the two men will be mentioned in brief. Subject E for the six months just preceding the experiment had lived upon a low-protein meat diet of but one meal a day, a diet which would represent not over 30 to 40 grams of protein and 1200–1800 calories of energy per day. On this diet he maintained his weight and performed his university duties. Subject H had lived upon a low-protein non-meat diet during the eight months preceding the experiment, a diet which would give a protein value of about 60 grams and an energy value of approximately 2000 calories per day.

Articles of Diet.—The food used in this investigation was purchased in quantities sufficient to last through the entire experiment. Each article of the diet was sampled and analyzed for total nitrogen.

[1] *Firenze*, 1889; from *Centralb. Physiol.*, 4, 862 (1890).
[2] *Skan. Archiv. Physiol.*, 7, 1 (1897).
[3] *Proc. Roy. Soc. Edinburgh*, 4 (1889).

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Crackers.—The graham crackers were obtained from the local dealers. After sampling they were kept in tin boxes.

Milk.—The milk was obtained from the dairy department of this University and analyses made from time to time showed the composition to have remained practically constant.

Butter.—The butter was obtained from the dairy department and was taken from a single "making" of butter, put up in one pound packages and preserved in a refrigerator. An analysis was made upon a sample taken at the time of making.

Water.—The ordinary distilled water was used such as is furnished to the general laboratories.

The Collection and Preservation of Excreta.—The urine was collected in twenty-four-hour periods and preserved in two-liter acid bottles coated on the inside with a thin layer of thymol. This thymol coating was produced by rinsing the bottle with a 10 per cent. alcoholic solution of thymol and allowing the alcohol to evaporate. Powdered thymol was added after the samples for analysis had been taken. When not in use the bottles were kept in a refrigerator.

The feces were collected in period samples and were passed into, and kept in, friction-top pails,[1] which were coated on the inside with a thin layer of thymol in the same manner as described in connection with the urine bottles. Charcoal was given, in gelatin capsules, at the beginning of each period and produced a very distinct separation zone.

Methods of Analysis.—The methods of analysis were as follows: total nitrogen, Kjeldahl; urea, Benedict-Gephart; ammonia, Folin; creatinine, Folin; creatine, Folin, Benedict and Myers.[2]

The Daily Routine.—The daily routine of the subjects was but partially prescribed, but their habits and duties resulted in the performance of a uniform amount of work each day. The prescribed routine was as follows: 7.00 A.M., urinate, defecate and weigh; 7.15 – 7.30, breakfast; 12.00—12.15 dinner; 5.00 P.M., supper; 10.00 P.M., retire.

The body weights were made upon the "stripped" subjects at 7.00 A.M., after they had urinated and defecated, the weights being made upon a platform balance accurate to 0.01 kilogram. The habits of the subjects were such that they defecated regularly at 7.00 A.M. (during the feeding periods), a fact which lends greater significance to the body weights as determined.

The amount of food required by each subject was determined by permitting a free choice of the various articles of food used in the experiment for a period of two days preceding the actual collection of data. The daily food ration was divided into three parts equal and eaten at the

[1] Howe, Rutherford and Hawk, THIS JOURNAL, 32, 1683 (1910).

[2] Methods used are referred to in Howe and Hawk, THIS JOURNAL, 33, 215 (1911)

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indicated meal hours. As a result of this selection Subject E consumed a slightly larger amount of food than did Subject H. Subject E took his water *between meals*, 250 cc. in the A.M., 250 cc. in the P.M. and 250 cc. at night while H took his *with meals*, 250 cc. with each meal.

Experimental.

Discussion of the Experiment upon Subject "E."

Preliminary Feeding Period.—Subject E at the beginning of this experiment had been maintaining his weight upon a low-protein meat diet, eating but one meal a day. He was placed upon the cracker-milk diet consisting of 600 grams of graham crackers, 1350 cc. of whole milk, 75 grams of butter and 700 cc. of water per day. Upon this diet the subject gained weight slightly and the nitrogen balance (Table V, p. 583) showed a retention of nitrogen. The preliminary feeding period was eight days in length, data being presented for the final four days of the period.

Nitrogen Partition.—The excretion of total nitrogen remained fairly constant from day to day, the average for the four days preceding the fast being 10.430 grams. The urea-nitrogen excretion paralleled that of the total nitrogen, the average being 9.070 grams of nitrogen per day. The percentage of total nitrogen occurring as urea nitrogen was 86.9 per cent. The ammonia nitrogen remained constant, giving an average of 0.112 gram per day, and representing an average of 1.0 per cent. of the total nitrogen. The creatinine nitrogen was also fairly constant, giving an average of 0.687 gram per day, a value which represented 6.5 per cent. of the total nitrogen.

Fasting Period.—The last food was taken at 5.00 P.M on May 13th and the fast was considered as beginning at 7.00 A.M. on the following day. The ordinary university duties were performed. The subject ingested water according to the following schedule: 7.00 A.M., 500 cc.; 9.00 A.M., 250 cc.; 12.00 M., 250 cc.; 3.00 P.M., 250 cc.; 9.00 P.M., 250 cc., making a total of 1500 cc. of water per day.

Extracts from the Diary of Subject E. May 14.—Slept well. Did not notice any hunger except at the regular meal hours and did not care much for water. *May 15:* Hunger not so noticeable this morning. However, I feel weak when climbing stairs. *May 16:* Slight ache in muscles of legs and back, have dizzy spells at times. *No hunger*, coated tongue and bad taste in mouth. *May 17:* Still have dizzy spells upon sudden movement. *May 18:* Weaker, dreamt of feasting. *May 19:* Rather tired, did not sleep well, again dreamed of eating. *May 20:* Mouth very stale, tongue heavily coated, do not feel much weaker than yesterday, cold feet and hands, otherwise O. K.

Body Weight.—The body weight fell from 74.22 kilograms (Table IV) on the morning of the beginning of the fast to 68.70 kilograms at the end

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TABLE I.—SUBJECT E.—GENERAL DATA.

Day of period.	Body weight. kgs.	Volume of urine. cc.	Specific gravity of urine.	Reaction of urine.	Total N. Grams.	Urea N. Grams.	Ammonia N. Grams.	Creatinine N. Grams.	Creatine N. Grams.	Per cent. of total nitrogen. Urea. N.	Ammonia. N.	Creatinine. N.	Creatine. N.
					Preliminary Feeding Period.								
1	74.10	1108	10205	ampho	10.353	9.039	0.105	0.700	...	87.3	1.0	6.8	..
2	74.18	990	10255	ampho	10.495	9.095	0.112	0.666	...	86.7	1.0	6.4	..
3	74.16	1040	1027	ampho	10.417	9.066	0.101	0.700	...	87.0	1.0	6.7	..
4	74.22	1030	1026	ampho	10.456	9.080	0.106	0.683	...	86.8	1.0	6.5	..
Av.					10.430	9.070	0.112	0.687		86.9	1.0	6.6	
					Fasting Period.								
1	73.32	678	10285	acid	10.072	8.732	0.288	0.350	0.269	86.7	2.8	3.5	2.67
2	71.98	1512	1014	acid	15.072	13.504	0.642	0.571	0.073	89.6	4.3	3.8	0.48
3	70.92	1463	10135	acid	14.463	12.692	0.862	0.574	0.089	87.7	6.0	4.0	0.62
4	70.24	960	10195	acid	13.080	11.245	1.201	0.538	0.068	85.9	9.2	4.1	0.52
5	69.61	1148	1013	acid	11.801	9.573	1.266	0.562	0.033	81.1	10.7	4.8	0.28
6	69.12	1137	10125	acid	11.214	8.897	1.373	0.540	0.022	79.3	12.2	4.8	0.20
7	68.70	1170	1013	acid	10.734	8.506	1.371	0.538	0.003	79.2	12.8	5.0	0.03
					Final Feeding Period.								
1	69.82	507	1025	acid	11.404	8.966	1.007	0.590	...	78.6	8.8	5.2	..
2	72.51	527	1028	acid	9.241	7.005	0.758	0.591	0.04	75.8	8.2	6.4	0.32
3	73.38	1558	1018	acid	10.219	7.525	1.413	0.763	...	73.6	13.8	7.5	..
4	73.68	1703	1020	ampho	10.355	8.909	0.301	0.761	...	86.3	2.9	7.4	..
5	73.40	2155	1017	ampho	11.508	9.360	0.988	0.687	...	81.3	8.6	6.0	..
6	73.40	1781	10205	ampho	10.827	9.129	0.510	0.682	...	84.3	4.6	6.3	..
7	73.56	1236	1024	ampho	11.507	10.072	0.239	0.647	...	87.5	2.1	5.6	..
8	73.44	1279	1024	ampho	12.094	10.550	0.310	0.669	...	87.2	2.6	5.5	..

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of the seven-day fast, this representing a loss of 5.52 kilograms or 7.4 per cent. of the original body weight. The greatest loss, 1.34 kilograms, occurred on the second day and the smallest loss, 0.42 kilogram, occurred on the seventh day.

Nitrogen Partition.—The average nitrogen output of the preliminary period was 10.430 grams. Under the influence of the first day of fasting this value was reduced to 10.072 grams, thus aggregating a loss of 0.358 gram in the total nitrogen output. A very pronounced *increase* occurred on the second day, the excretion rising from 10.072 grams on the first day to 15.072 grams on the second day or an increase of 5 grams of nitrogen. From the second day on the nitrogen excretion fell, the variation from day to day becoming less pronounced as the fast progressed. The quantity of nitrogen excreted on the last day was greater than the average daily output of the feeding period or of any individual day of the preliminary period.

The urea-nitrogen excretion followed in general that of the total nitrogen. The percentage of the total nitrogen which appeared as urea varied, however, increasing from 86.7 per cent. on the first day to 89.6 per cent. on the second day and then decreasing steadily to the end of the fast, the percentage on the last day (79.2 per cent.) being the lowest value for the period.

The ammonia-nitrogen excretion was higher at all times during the fast than the average of the feeding period, 0.112 gram per day. The minimum excretion was one of 0.288 gram which occurred on the first day and the maximum excretion was one of 1.373 grams which occurred on the sixth day, there being a rapid increase during the first four days, after which the increase was less pronounced. The relative ammonia-nitrogen excretion increased from the average of 1 per cent. of the total nitrogen for the feeding period to 2.8 per cent. on the first day of the fast and then increased steadily to 12.8 per cent. on the last day.

The creatinine-nitrogen excretion dropped from the average feeding value of 0.687 gram to 0.350 gram on the first day of the fast, rising to 0.571 gram on the second day, and from there on remained practically constant throughout the fast. The relative creatinine-nitrogen excretion decreased from the average value of the feeding period (6.6 per cent. to 3.5 per cent.) on the first day of the fast and then increased very gradually for three days, after which it assumed a higher level and remained practically constant on this plane during the last three days of the fast.

On the first day of the fast there was a very marked excretion of creatine, 0.269 gram. The data from the following day present a much lower value, 0.073 gram, which increased on the third day to 0.089 gram and the values then decreased to the end of the fast, the output for the final day being 0.003 gram. The relative creatine output followed that of the abso-

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lute excretion, being highest on the first day, falling on the second and rising again on the third day, the lowest percentage occurring on the last day.

Final Feeding Period.—The amounts of food ingested varied from day to day, as shown in Table V, the greatest changes in the diet being in the quantities of milk consumed, although there was an increase in both the crackers and the butter. The nitrogen intake ranged from 13.465 grams on the first day of feeding to 21.107 grams on the second day. There was an increased water ingestion of 300 cc. during this period, the water being taken at 10.00 A.M., 3.00 P.M., and 9.00 P.M., *i. e.*, between meals, as in the preliminary feeding period. As a result of this diet the subject regained 85 per cent. of his body weight in three days and held the same during the remainder of the experiment (see Table IV). The greatest increase in body weight occurred on the second day, when the weight rose from 69.82 kilograms to 72.51 kilograms or an increase of 2.69 kilograms in one day. For further discussion see p. 580.

Nitrogen Partition.—The total nitrogen excretion (Table I, p. 573) instead of varying with the fluctuations in the diet remained fairly constant. The lowest excretion of nitrogen, 9.241 grams, occurred on the second day when the ingestion of food was the greatest, 21.107 grams of nitrogen (Table V), and the highest excretion (12.094 grams) occurred on the eighth day of feeding when the ingestion was lowest, 14.043 grams of nitrogen. This was the same diet as that fed during the preliminary feeding period. The urea-nitrogen excretion varied with the total nitrogen; relatively, however, there were more marked changes (Table I, p. 573). The percentage of the total nitrogen which appeared as urea nitrogen decreased during the first three days of the feeding period from 78.6 per cent. to 73.6 per cent., these values all being lower than the lowest percentage output of the fasting period. From this point there was a general tendency toward a rather pronounced increase, the final day of the feeding period showing an output of 87.2 per cent. of the total nitrogen in the form of urea. This figure was about normal (86.9 per cent.) for this subject. The ammonia-nitrogen excretion also showed fluctuations during this period, being low when the urea was high and *vice versa*. A low (0.301 gram) ammonia excretion occurred on the fourth day, being preceded by a high excretion. This high excretion of 1.413 gram of ammonia nitrogen was the maximum for the period, the minimum (0.239 gram) occurring on the seventh day. For the first two days the creatinine-nitrogen excretion remained near the level of that of the fasting period, the output being 0.538 gram on the last day of the fast as against an average of 0.590 gram for the first two days of the feeding period. On the third and fourth days there was a distinct rise to an average of 0.762 gram, after which the excretion fell, the average output for the

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fifth and sixth days being 0.684 gram. The average daily excretion for the final four days of the period (0.671 gram) was very close to the average daily output (0.687 gram) for the preliminary period.

Discussion of the Experiment upon Subject H.

Preliminary Feeding Period.—Subject H, previous to the experiment, had been living upon a more normal diet than Subject E. The diets differed in that Subject H had ingested no meat for a period of eight months, his diet being distinctly so-called "vegetarian" in character. The diet in the preliminary feeding period was also slightly different and consisted of 450 grams of graham crackers, 1350 cc. of whole milk, 75 grams of butter and 750 cc. of water, furnishing a nitrogen value of 12.138 grams per day. On this diet he maintained an almost constant body weight and the nitrogen balance (see Table V, p. 583) showed but slight variations.

Nitrogen Partition.—The excretion of total nitrogen remained nearly constant throughout the preliminary feeding period. The average excretion for the four days was 9.814 grams per day. The absolute urea-nitrogen excretion followed that of the total nitrogen, the average being 8.520 grams per day. Relatively, the variations ranged between 83.4 per cent. of the total nitrogen on the first day and 84.6 per cent. on the second day, the average for the period being 84.3 per cent. The average ammonia-nitrogen excretion for the period was 0.271 gram per day. The relative excretion of ammonia nitrogen varied slightly, decreasing from a value of 3.5 per cent. on the first day to 2.5 per cent. on the fourth day, the average for the period being 2.7 per cent. The creatinine-nitrogen excretion remained practically constant throughout the four days, the average being 0.639 gram per day. Relatively the average excretion was 6.5 per cent of the total nitrogen.

Fasting Period.—The fast of Subject H began under the same conditions with regard to the day, etc., as that of Subject E, see p. 572. Subject H, however, consumed 250 cc. more water per day than did Subject E.

Extracts from the Diary of Subject H.—May 14: Feeling well, slight lassitude. *May 15:* Felt well all day, *no hunger*, tongue coated, bad taste in mouth. *May 16:* Felt well all day, slightly weak, *no hunger*. *May 17:* Quite weak this morning, slept well, dizzy spell in afternoon, *no hunger*. *May 18:* Felt well all day and although I am weak, it is not as great an exertion to walk as it was at first. *No hunger*. *May 19:* Feeling well, in very good spirits only weak when it comes to any exertion. *No hunger*. *May 20:* Weak, slept well. *No hunger*.

Body Weight.—The body weight fell from 70.30 kg. on the morning of the day the fast began to 64.94 kg. at the end of the fast or a loss of

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TABLE II.—SUBJECT H.—GENERAL DATA.

Day of period.	Body weight. kgs.	Volume of urine. cc.	Specific gravity of urine.	Reaction of urine.	Total N. Grams.	Urea N. Grams	Ammonia N. Grams.	Creatinine N. Grams.	Creatine N. Grams.	Per cent. of total nitrogen. Urea N.	Ammonia N.	Creatinine. N.	Creatine. N.
					Preliminay Feeding Period.								
1	70.36	770	1031	ampho	9.852	8.218	0.344	0.630	...	83.4	3.5	6.4	..
2	70.44	800	1027	ampho	9.987	8.452	0.259	0.636	...	84.6	2.6	6.4	..
3	70.36	770	1029	ampho	9.615	8.121	0.238	0.647	...	84.5	2.6	6.7	..
4	70.30	790	1029	ampho	9.801	8.286	0.243	0.641	...	84.5	2.5	6.5	..
Av.					9.814	8.520	0.271	0.639		84.3	2.7	6.5	
					Fasting Period.								
1	69.50	651	10235	acid	8.338	6.999	0.330	0.547	0.012	83.9	3.9	6.6	0.14
2	68.22	1150	1014	acid	11.097	9.565	0.632	0.580	0.037	86.2	5.7	5.2	0.33
3	67.12	1320	10145	acid	12.821	10.898	1.097	0.555	0.066	85.0	8.6	4.3	0.52
4	66.53	890	10195	acid	12.116	9.705	1.434	0.539	0.089	80.1	11.8	4.4	0.73
5	65.90	1132	10145	acid	11.176	8.727	1.541	0.520	0.036	78.1	13.8	4.6	0.32
6	65.28	1098	10115	acid	10.407	7.892	1.432	0.554	0.053	75.8	13.8	5.3	0.51
7	64.94	939	10165	acid	10.158	7.700	1.411	0.509	0.033	75.8	13.9	5.0	0.33
					Final Feeding Period.								
1	65.72	530	1018	acid	10.996	8.628	1.025	0.355	0.207	78.5	9.3	3.2	1.88
2	68.98	550	1019	acid	10.919	8.647	0.919	0.349	0.273	79.2	8.4	3.2	2.5
3	69.50	870	10275	ampho	9.687	6.684	1.610	0.611	0.025	69.0	16.6	6.3	0.26
4	69.69	1035	1025	ampho	8.665	7.119	0.340	0.615	0.033	82.2	3.9	7.1	0.38
5	70.28	1491	1020	ampho	9.244	7.707	0.223	0.646	...	83.4	2.4	7.0	..
6	69.43	1386	1021	ampho	8.602	7.060	0.256	0.606	...	82.1	3.0	7.0	..
7	68.56	1213	10235	ampho	9.199	8.019	0.228	0.549	...	87.2	2.5	6.0	..
8	68.10	856	10295	ampho	10.104	8.313	0.242	0.589	...	82.3	2.4	5.8	..

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5.36 kg. in the seven days. The loss in body weight on the first day, 0.80 kg., was followed by a much greater loss, 1.28 kg., on the second day, after which the losses from day to day became less and less as the fast progressed until the end of this period, when the minimum loss, 0.34 kg., occurred.

Nitrogen Partition.—The average output of nitrogen during the preliminary period was 9.814 grams per day. Under the influence of the first day of fasting 8.338 grams were excreted, this being the minimum daily output recorded during the course of the experiment. During the two following days, the nitrogen excretion increased to the maximum, 12.821 grams, and then decreased gradually throughout the remainder of the fast. An excretion of 10.158 grams of nitrogen occurred on the last day; this value was higher than the total nitrogen excretion for any day during the feeding period (see discussion of data, p. 588).

The urea-nitrogen excretion followed that of the total nitrogen. The percentage of the total nitrogen which was excreted as urea nitrogen fell below the average of the feeding period (84.3 per cent.) on the first day (83.9 per cent.), then rose on the second day (86.2 per cent.) and decreased from this point to the end of the fast. The highest percentage (86.2 per cent.) occurred on the second day and the lowest (75.8 per cent.) on the sixth and seventh days.

The absolute excretion of ammonia nitrogen increased from day to day until the fifth day and then decreased slightly during the next two days, the excretion being 0.330 gram for the first day, 1.541 gram for the fifth day and 1.432 and 1.411 gram for the final days. Relatively, the percentage of the total nitrogen excreted as ammonia nitrogen increased from day to day, the lowest percentage being 3.9 on the first day and the highest being 13.9 on the last day of the fast.

The creatinine-nitrogen excretion dropped on the first day from the average of the feeding period (0.639 gram) to 0.547 gram and fluctuated but slightly during the remainder of the fast. The relative creatinine-nitrogen excretion decreased from 6.5 per cent. on the first day to 4.3 per cent. on the third day and then increased to 5.3 per cent. on the sixth day and fell slightly to 5.0 per cent. on the last day of the fast.

Creatine appeared on the first day of the fast and the data from the creatine nitrogen show an increase for the first four days from 0.012 gram of nitrogen on the first day to 0.089 gram on the fourth day and then a decrease during the remainder of the fast, to 0.033 gram on the seventh day. The percentage of the total nitrogen excreted in the form of creatine nitrogen varied, the maximum being 0.73 per cent. on the fourth day and the minimum 0.14 per cent. on the first day.

Final Feeding Period.—The general conditions as outlined for Subject E obtained for Subject H during this period. Subject H, however,

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selected a diet furnishing less nitrogen, he consumed less milk and also took larger quantities of water, see Tables V and VI, pp. 583 and 587. With this diet, Subject H made very rapid gains in body weight and recovered his original weight in five days. At this point, the original uniform diet was ingested, which dietary change was accompanied by a loss in weight, due probably to the fact that the low ration was insufficient for this organism just recovering from a seven-day fast. The largest gain in weight occurred during the second day, the body weight increasing from 65.72 kilograms to 68.98 kilograms or a gain of 3.26 kilograms in one day.

Nitrogen Partition.—The excretion of nitrogen varied within rather narrow limits as compared with the fluctuations in the quantity of nitrogen ingested (see Tables II and V, pp. 577 and 583). The urea-nitrogen excretion followed that of the total nitrogen. Relatively, the urea nitrogen increased from day to day; the lowest percentage (69.0) occurred on the third day, an output which was the lowest recorded at any time during the experiment. The highest percentage (87.2 per cent.) occurred on the seventh day of the feeding period. The excretion of ammonia nitrogen decreased with the ingestion of food but exhibited marked fluctuations. On the third day the excretion rose from 0.919 gram to 1.610 grams, this increase of 0.691 gram being greater than that occurring on any day during the fast. An equally pronounced drop resulted on the following day, the excretion being 0.340 gram. The excretion for the fifth day was 0.223 gram and the ammonia-nitrogen output remained practically at this level during the remainder of the period. The percentage of the total nitrogen excreted as ammonia showed similar fluctuations, being high on the third day, 16.6 per cent., decreasing on the fourth day to 3.9 per cent., and continuing on a similarly low level. Upon the ingestion of food, the creatinine-nitrogen excretion fell from 0.509 gram to 0.355 gram and remained low for two days. The excretion regained approximately the preliminary feeding level on the third day and maintained this level during the remainder of the experiment. Similar changes occurred in the relative creatinine-nitrogen excretion, which dropped to 3.2 per cent. on the first day and rose to 6.3 per cent. on the third day. This level was virtually maintained throughout the succeeding experimental days. The excretion of creatine noted during the fast continued during the first four days of feeding, the highest creatine-nitrogen excretion of the experiment, 0.273 gram, occurring on the second day of the feeding period. The excretion decreased on the third day and disappeared on the fifth day. It is an interesting fact that an average of over 2 per cent. of the total nitrogen output was excreted as creatine upon the first two days of the feeding period.

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General Discussion.

The data from the fasts of two men,[1] Subjects E and H, have been presented. These men had been, previous to the beginning of the experiment, living upon different diets; the one, Subject E, upon a low-protein meat diet of but one meal a day, and the other, Subject H, upon a medium low-protein non-meat diet taken in the normal manner, *i. e.*, three meals a day. The men were very similar as to physique and temperament and their daily duties were, in a sense, similar. Thus, we approach a fast with two subjects whose dietary habits are different, through a preliminary feeding period in which the same diet was fed but in which water was taken in the case of Subject H, with meals, and in the case of Subject E, between meals. Under these conditions, they experienced a fast of seven days, the results of which are very similar as regards body weight changes and the partition of urinary nitrogen. Following the fasts came feeding periods during which the diet varied quantitatively but not qualitatively.

Body Weights.—The possibility of error in the determination of the body weights was reduced to a minimum, since practically all the interfering factors, such as the retention of urine or feces, changes in the weight of the clothes etc., were eliminated, consequently the fullest credence may be given the results. The daily variations in the body weights of the two subjects were very similar. Subject E sustained the greatest total loss, 5.52 kilograms, for the seven days, against a loss of 5.36 kilograms for Subject H during the same time. Subject H, however, experienced the greatest percentage loss, this being 7.6 per cent. of the body weight as compared with a loss of 7.4 per cent. for Subject E. The actual daily losses as well as the daily percentage losses for the two subjects show but slight variations, the former values being slightly higher for subject E, whereas, the latter values were a trifle higher for Subject H. In both cases a smaller loss in body weight occurred on the first day as compared with the losses on the second and third days. After the second day, which was the day of maximum loss, the loss per day became gradually less, the minimum occurring on the last or seventh day in each case. The percentage loss per day shows similar variations to that of the absolute loss.

An interesting comparison may be made of the daily losses for the first seven days of the more important fasts recorded in the literature. A consideration of the appended table (Table III, p. 581) will show that changes in body weight similar to those just discussed have occurred in previous fasts although the gradual decrease in the daily loss was not so regular as in the experiments reported by us. The experiments in which the losses in body weight more nearly approach those of our ex-

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TABLE III.—LOSSES IN BODY WEIGHT.

	Johanson, Landergren, Sonden and Tigerstedt.[1]	Lehmann, Müller, Munk, Senator, Zunz.[2]		Landergren.[3]	At Paris.[4]	At Milan.[4]	Luciani.[5]	Ajello and Sofaro.[6]	Paton and Stockman.[7]	Benedict.[8]			Cathcart.[9]	Howe, Mattill and Hawk.	
										S. A. B.					
	J. A.	Cetti.	Breithaupt.	XI.	Succi.	Succi.	Succi.	Succi.	Jacques.	73.	75.	Average.	Beauté.	E.	H.
Wt. on last day of food.....	67.80	57.00	60.07	78.60	..	..	63.30	63.60	62.01	59.13	59.52	..	65.61	74.22	70.30
Loss 1st day.....	1.63	0.55	0.55	0.60	..	..	0.90	..	1.33	1.17	0.04	1.05	1.04	0.90	0.80
Loss 2nd day....	0.92	0.94	0.63	1.77	3.60	1.55	1.40	1.80	0.94	0.69	0.72	1.00	0.85	1.34	1.28
Loss 3rd day.....	0.75	1.08	0.77	1.00	0.40	0.80	1.20	1.20	0.51	0.84	0.69	0.79	0.95	1.06	1.10
Loss 4th day.....	1.03	0.98	0.95	0.80	1.00	0.75	+0.10	0.80	+0.01	0.78	0.89	0.88	0.81	0.68	0.59
Loss 5th day.....	0.68	0.85	0.20	..	0.60	0.50	0.60	0.70	0.26	0.67	0.45	0.56	0.55	0.63	0.63
Loss 6th day.....	..	0.25	0.52	..	0.30	0.85	0.65	0.90	0.62	..	0.39	0.39	0.58	0.49	0.62
Loss 7th day.....	..	0.00	..	..	0.10	0.55	..	0.70	+0.20	..	0.50	0.50	0.60	0.42	0.34

[1] *Skan. Archiv. Physiol.*, 7, 29 (1897).
[2] *Virchow's Archiv.*, 131, suppl. (1893).
[3] *Skan. Archiv. Physiol.*, 14, 152 (1903).
[4] Taken from *Carnegie Pub.*, 77, 1907.
[5] *Das Hungern, Leipzig*, 1890.
[6] *La Riforma Medica*, 9, 2, 542 (1893).
[7] *Proc. Roy. Soc. Edinburgh*, 16, 121 (1888–1889).
[8] *Carnegie Pub.*, 77 (1907).
[9] *Biochem. Z.*, 6, 109 (1907).

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periments in regularity were two of the fasting tests in which Succi served as subject.

Due to the varying diet, the changes in the body weights of Subjects E and H during the period of regeneration were variable. The most significant results are those of the first three days which indicate a small increase in the body weight on the first day of food followed on the second day by a very pronounced increase amounting to 2.69 kilograms and 3.26 kilograms for Subjects E and H respectively. On the third day, a much smaller increase in body weight occurred and the data show the daily increases for the remaining days of the period to have been on this latter plane. During the last three days of the regeneration period, Subject H ingested the constant diet previously fed during the preliminary period, a diet which apparently was not sufficient for him under the circumstances, as indicated by a daily loss in weight. Subject E also returned to the original diet for a single day during which a small loss in weight was recorded.

TABLE IV.—CHANGES IN BODY WEIGHT AND CREATININE COEFFICIENTS.

	Subject E.				Subject H.			
Day of period.	Body weight. Kg.	Daily loss or gain in weight. Kg.	Per cent.[1] daily loss or gain in weight.	Creatinine coefficient. Mg.	Body weight. Kg.	Daily loss or gain in weight. Kg.	Per cent.[1] daily loss or gain in weight.	Creatinine coefficient. Mg.
			Preliminary Feeding Period.					
4	74.22	..	..	9.2	70.30	..	..	9.1
			Fasting Period.					
1	73.32	— 0.90	— 1.21	4.8	69.50	— 0.80	— 1.14	7.9
2	71.98	— 1.34	— 1.79	7.9	68.22	— 1.28	— 1.82	8.5
3	70.92	— 1.06	— 1.43	8.1	67.12	— 1.10	— 1.56	8.3
4	70.24	— 0.68	— 0.92	7.7	66.53	— 0.59	— 0.84	8.1
5	69.61	— 0.63	— 0.85	8.1	65.90	— 0.63	— 0.90	7.9
6	69.12	— 0.49	— 0.66	7.8	65.28	— 0.62	— 0.88	8.5
7	68.70	— 0.42	— 0.57	7.8	64.94	— 0.34	— 0.48	7.8
Total.....		— 5.52	— 7.44			— 5.36	— 7.62	
			Final Feeding Period.					
1	69.82	+ 1.12	+ 1.49	8.4	65.72	+ 0.78	+ 1.11	5.4
2	72.51	+ 2.69	+ 3.62	8.1	68.98	+ 3.26	+ 4.64	5.1
3	73.38	+ 0.87	+ 1.17	10.4	69.50	+ 0.52	+ 0.74	8.8
4	73.68	+ 0.30	+ 0.40	10.3	69.69	+ 0.19	+ 0.27	8.8
5	73.40	— 0.28	— 0.38	9.3	70.28	+ 0.59	+ 0.84	9.2
6	73.40	0.00	....	9.3	69.43	— 0.85	— 1.21	8.7
7	73.56	+ 0.16	+ 0.22	8.8	68.56	— 0.87	— 1.24	8.0
8	73.44	— 0.12	— 0.16	9.1	68.10	— 0.46	— 0.65	8.6

[1] The per cent. *loss* in body weight during the fasting period is calculated on the basis of the body weight on the last day of the preliminary period, whereas the *gain* during the final feeding period is calculated on the basis of the weight on the last day of the fast.

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TABLE V.—NITROGEN BALANCES.

Day of period.	Subject E. Nitrogen in urine. Grams.	Subject E. Nitrogen in urine + feces. Grams.	Subject E. Nitrogen in food. Grams.	Subject E. Nitrogen balance. Grams.	Subject H. Nitrogen in urine. Grams.	Subject H. Nitrogen in urine + feces. Grams.	Subject H. Nitrogen in food. Grams.	Subject H. Nitrogen balance. Grams.
				Preliminary Feeding Period.				
1	10.353	12.485	14.043	+1.556	9.852	11.828	12.138	+0.310
2	10.495	12.627	14.043	+1.416	9.987	11.953	12.138	+0.185
3	10.417	12.549	14.043	+1.494	9.615	11.681	12.138	+0.457
4	10.456	12.588	14.043	+1.455	9.801	11.762	12.138	+0.371
Av.,	10.430	12.396		+1.480	9.814			+0.331
				Fasting Period.				
1	10.072	10.182	....	—10.182	8.338	8.483	....	—8.483
2	15.072	15.182	....	—15.182	11.097	11.242	....	—11.242
3	14.463	14.573	....	—14.573	12.821	12.966	....	—12.966
4	13.080	13.190	....	—13.190	12.116	12.261	....	—12.261
5	11.801	11.911	....	—11.911	11.176	11.321	....	—11.321
6	11.214	11.320	....	—11.320	10.407	10.552	....	—10.552
7	10.734	10.840	....	—10.840	10.158	10.303	....	—10.303
				Final Feeding Period.				
1	11.404	14.697	13.465	—1.231	10.996	13.265	14.988	+1.723
2	9.241	12.534	21.107	+8.573	10.919	13.188	18.800	+5.612
3	10.219	13.512	19.817	+6.305	9.687	11.956	14.100	+2.144
4	10.355	13.648	18.820	+4.828	8.665	11.934	14.100	+2.166
5	11.508	14.801	18.800	+3.999	9.244	11.513	18.800	+7.287
6	10.827	14.120	17.740	+3.620	8.602	10.871	12.793	+1.922
7	11.507	14.800	15.242	+0.442	9.199	11.468	12.138	+0.690
8	12.094	15.387	14.043	—1.344	10.104	12.373	12.138	—0.235

A consideration of the nitrogen balances during the feeding periods (Table V, p. 583) and the changes in body weights (Table IV, p. 582) present some very interesting facts. On the first day, Subject E showed a negative nitrogen balance of 1.231 grams with an increase in weight of 1.12 kilograms, denoting a storage of material other than protein and probably in large part water. Subject H, on the other hand, had a distinct positive nitrogen balance, 1.723 grams, with a much lower gain in body weight, 0.78 kilogram. The total nitrogen excretion in both cases was quite similar, *i. e.*, 11.404 grams for Subject E and 10.996 grams for Subject H. Upon the following day with an ingestion of a diet containing 21.107 grams of nitrogen and 3750 cc. of water, Subject E showed a nitrogen balance of +8.573 grams and a gain of 2.69 kilograms in body weight. On the other hand, Subject H, upon an ingestion of 18.800 grams of nitrogen and 3566 cc. of water yielded a nitrogen balance of +5.612 grams, and gained 3.26 kilograms in body weight. Benedict[1] observed a pronounced nitrogen storage under similar conditions after

[1] *Carnegie Pub.*, **77**, 534.

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the third day. The urine volumes of the two subjects were almost identical, 527 cc. for Subject E and 550 cc. for Subject H.

The phenomena just mentioned, we have interpreted as indicating a marked retention of water which must have been held as water of combination resulting from the renewed activities of the cells inasmuch as throughout the fast the subjects ingested a uniform and liberal quantity of water each day. A certain small part of this marked increase in weight was, of course, due to the rapid formation of glycogen, since the glycogenic function is markedly stimulated when food is taken after a fast.[1] The quantities formed, however, according to Benedict's figures, which show a maximum formation of 217 grams of glycogen on the third day, are not such as would account for any large part of the observed excessive increase in body weight. It must be further borne in mind that the general anabolic activities of the organism are, of course, greatly stimulated during such a "post-fasting" feeding period. Pashutin[2] has recorded data from lower animals which show a marked increase in weight on the first and second days of feeding after fasting. Benedict, in his experiments in feeding after fasting, does not record any such marked increases in body weight as those reported by us. His subjects received but small amounts of food during the early days (three) of the regeneration period and gave negative or low positive nitrogen balances for that period. The conditions were different in the case of our subjects inasmuch as these men ingested the *maximum amount of food for any individual day upon the second day after the fast.* It is of interest that the subjects experienced no discomfort following the ingestion of the excessive diet so soon after the close of the fast. Furthermore, no undesirable results of any kind were noted in connection with this unusual dietary régime. It is, of course, customary to use great care in the feeding of fasting subjects immediately subsequent to the fast. Pre-digested material is many times ingested in small quantity and under certain conditions nothing other than simple fruit juices are permitted the person who is in the initial stages of "breaking" the fast. With these facts in mind it is of added significance that the subjects of our experiments experienced no ill effects from the ingestion of the customary *full ration* immediately subsequent to the fast. *In fact, H ingested upon the first day of feeding, 15 grams of nitrogen as against 12 grams during the period preceding the fast.*

As a result of the ingestion of food as already indicated Subject E *regained 90 per cent. of his lost body weight in four days* and then maintained a practically constant body weight during the remaining four days of

[1] Benedict, *Carnegie Pub.*, 77, 531; Schultz and Mangold, *Arch. ges. Physiol.*, 114, 419 (1906).

[2] *Loc. cit.*

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the experiment. After five days of feeding, Subject H had practically *regained his original body weight, i. e., 99.6 per cent.* He had, however, regained only about one-third of the nitrogen lost during the fast. On the sixth day of feeding H returned to the same diet as that consumed before the fast. Under these conditions he gradually lost weight and the nitrogen balance indicated that the body was not receiving sufficient nitrogen to maintain its functional activities and normal body weight. This phenomenon of increased food requirement has been recorded by Pashutin[1] in experiments on rabbits. Howe and Hawk, in the case of the dog, found that the ingestion of the normal quantity of food resulted in a very slow restoration of the lost nitrogen and that the body weight remained practically constant although when the quantity of food ingested was increased, the nitrogen loss and the weight were restored rapidly. This same condition appears to exist in our experiment, for upon the increased diet, the body weight increased regularly and large amounts of nitrogen were retained, but upon return to the diet of the preliminary period, there was a loss of nitrogen and a decrease in body weight.

The process of regeneration, then, seems to have been in a general way accompanied by a rapid formation of glycogen, the retention of water and a pronounced retention of nitrogen during the earlier days, each of these factors becoming gradually less in evidence as the feeding period progressed. The pronounced retention of nitrogen may be considered to represent the formation of the nitrogenous tissue through the instrumentality of the marked stimulation of the anabolic changes subsequent to the fast. The body weight was restored very quickly but there were not concomitant changes in body weight for the amounts of nitrogen stored. For example, on the second day of the feeding period, Subject H ingested 18.8 grams of nitrogen, gained 3.26 kilograms in body weight and stored 5.612 grams of nitrogen, whereas, on the fifth day on a nitrogen ingestion, identical with that mentioned above, he stored 30 per cent. more nitrogen (7.287 grams), notwithstanding the fact that he gained less than 1/5 as much in body weight (0.59 kg.) as upon the second day. Upon the reduction of the diet to that consumed before the fast the body weight decreased about as rapidly, on the average, as it did during the fast, when no food was received. The nitrogen balance during this time tended toward a negative condition showing that the requirements of the body were greater than before the fast and that more nitrogen must be ingested to maintain the body in nitrogen equilibrium and at a constant weight.

Ingestion and Elimination of Water.—Data regarding the quantity of urine voided per day and the specific gravity of these samples are given in Tables I and II, pp. 573 and 577. The volume of the urine excreted

[1] *Loc. cit.*

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is influenced among other things by the amount of water consumed, the work performed and the weather conditions. In these experiments, the quantity of water consumed was maintained as a constant for each man, the amount and nature of the work performed from day to day was uniform and the weather conditions during the fast were fortunately very regular. The extreme variation in the temperature[1] was 7.5° F. (60° F.–67.5° F.) or, excluding the first day, 4.7° F. (60° F.–64.7° F.). The humidity[2] was also quite constant after the first two days when the mean humidity was 80 and 74.3, respectively. The average for the remaining five days was 63.6, the extremes being 66 and 59.6 on the sixth and seventh days respectively.

Under these very favorable conditions the urine volumes of the two subjects were relatively similar, being low on the first day of the fast and rising to a higher plane on the second and third days, dropping on the fourth day and then rising again on the fifth to remain nearly constant through the remainder of the fast. The cause for the decreased volume on the fourth day is not apparent, for the conditions existing on this day were almost identical with those of the previous day and yet both subjects showed the same phenomenon. A comparison of these data with those of other investigators,[3] especially those of Benedict, who has made the most accurate determinations, is hardly possible on account of the differences in the water ingestion. The factor of work which enters into our experiment increased in general the insensible elimination of water and the specific gravities and urine volumes were thereby affected.

In Table VI, p. 587, are given data regarding the percentage of the ingested water which was eliminated by way of the kidneys. We see, in the first place, that this percentage was throughout the fast and the preliminary feeding period rather higher for E than for H. For example, E's preliminary water value was about 55 per cent., whereas H's was about 40 per cent. When we pass to the fast we find the water percentages for E are still above those for H. Upon the first day of the fast, 67.8 per cent. of the ingested water (1000 cc.) was eliminated by E, whereas H eliminated but 37.2 per cent. of the volume (1750 cc.) ingested, and a similar relation, although somewhat less accentuated, held for each individual day of the fasting period. Benedict[4] found, when the volume of water taken by fasting men was small, that "the urine volume may exceed it several times," whereas, "when the volume of drinking water is over 1000 cc., the volume of the urine is not far from

[1] The data regarding the weather were obtained from the weather records of the Ill. Agr. Exp. Sta. through the kindness of Prof. J. G. Mosier.

[2] The humidity used was the average of the three daily observations taken at 7.00 A.M., 2 P.M. and 9 P.M.

[3] *Loc. cit.*

[4] *Carnegie Pub.*, 77, 351.

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that of the water consumed." In our experiments we found only one instance in which the volume of urine exceeded that of the ingested water and that was an excess of only 12 cc. on a basis of 1500 cc. It will be further noted in our experiments that the largest water ingestion was not followed by the most complete water elimination as found by Benedict. For example, Subject H ingested 1750 cc. of water per day as against 1500 cc. for Subject E and eliminated from 12–35 per cent. *less* than Subject E. In other connections one of us[1] has shown that under conditions of *normal nutrition*, a copious water ingestion will be followed by the elimination of a *higher percentage* of that water in the urine than would be excreted upon a lower-water ration. This has been shown to hold true for several subjects. The situation is materially altered, however, when we cause a man to ingest water *unaccompanied by food.*

TABLE VI.—PERCENTAGE WATER ELIMINATION.

	Subject E.				Subject H.			
Day of period.	Urine volume. cc.	Water ingested. cc.	Water + water in milk[2] ingested. cc.	Per cent. of ingested water eliminated through kidneys.	Urine volume. cc.	Water ingested. cc.	Water + water in milk[2] ingested. cc.	Per cent. of ingested water eliminated through kidneys.
			Preliminary Feeding Period.					
1	1108	700	1875	59.1	770	750	1925	40.0
2	990	700	1875	52.8	800	750	1925	41.6
3	1040	700	1875	55.5	770	750	1925	40.0
4	1030	700	1875	55.0	790	750	1925	41.0
			Fasting Period.					
1	678	1000	..	67.8	651	1750	..	37.2
2	1512	1500	..	100.8	1150	1750	..	65.7
3	1463	1500	..	97.5	1320	1750	..	75.4
4	960	1500	..	64.0	890	1750	..	50.9
5	1148	1500	..	76.5	1132	1750	..	64.7
6	1137	1500	..	75.8	1098	1750	..	62.7
7	1170	1500	..	78.0	939	1750	..	53.7
			Final Feeding Period.					
1	507	1000	2175	23.3	530	1100	2492	21.3
2	527	1750	3750	14.0	550	2000	3566	15.4
3	1558	1250	3120	49.9	870	1250	2424	35.9
4	1703	500	2545	66.9	1035	1000	2175	47.6
5	2155	500	2066	104.3	1491	750	2316	61.3
6	1781	1000	2827	63.0	1386	750	1925	72.0
7	1236	1000	2392	51.7	1213	750	1925	63.0
8	1279	1000	2175	58.8	856	750	1925	44.5

It seems rather clear that the whole question of the percentage of water which will be eliminated by a man by way of the kidneys is influenced,

[1] Hawk, University of Pennsylvania, *Medical Bulletin*, 18, 7 (1905); Rulon and Hawk, *Archives Internal Medicine*, 1911,

[2] Water content of milk taken as 87 per cent.

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to a surprising degree, by the factor of individuality. This has been clearly demonstrated by one of us[1] in experiments which go to show that two men of approximately the same age, weight and lung capacity, maintained upon the same constant diet and drinking precisely the same volume of water daily may nevertheless excrete surprisingly different volumes of urine. Therefore, in the fasting study under consideration in the present paper it may, of course, very well be that the element of individuality is the basic factor leading to the uniformly higher percentage water elimination for one subject above that noted for the other subject.

The changes in the urine volumes during the feeding period were most marked during the first two days, when they were very low. In the case of Subject E, with water ingestions (water plus the water in the milk) of 2175 cc. and 3750 cc., the urine volumes were but 507 and 527 cc. or but 23.3 per cent. and 14.0 per cent. of the water ingested. The same phenomenon existed with H. On water ingestions of 2492 cc. and 3566 cc., but 530 cc. and 550 cc. of urine were excreted, these values being only 21.3 per cent. and 15.4 per cent. respectively of that ingested. This condition represents a very marked retention of water, as already mentioned. There was also a noticeable retention of water in the case of Subject H upon return to the original diet during the last three days. This retention was accompanied by a negative nitrogen balance.

Distribution of Nitrogen. Total Nitrogen.—The excretion of total nitrogen has been studied in nearly all the experiments reported upon fasting man. A summary of the total nitrogen data for the first seven days of fasting from the more important fasts is contained in Table VII, p. 589. These data, with the exception of those for Subjects E and H, were collected from subjects *not performing manual labor.*[3] A comparison of the data there presented shows in general a drop in the excretion of nitrogen on the first day of the fast above that excreted on the last day of food, followed by a rise in the excretion, which reached its maximum on the second or third day. Prausnitz[3] made a study of the nitrogen excreted during the first two days of fasting and he found in general, an increased elimination on the second day. Neither in these experiments by Prausnitz nor in those of the investigators tabulated did the maximum excretion exceed that of the last feeding day by any great amount. In fact, in the majority of the cases reported, it was less than that of the feeding period. The average results of Benedict's[4] experiments have also been incorporated in the table and these show similar

[1] Hawk, *Am. J. Physiol.*, 10, 125 (1903).
[2] The subject J. A. did light muscular work in a respiration apparatus.
[3] *Z. Biol.*, 29, 151 (1893).
[4] *Loc. cit.*

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TABLE VII.—EXCRETION OF NITROGEN.

Day of fast.	Subject	Investigator.	Johansson, Landergreen, Sonden and Tigerstedt.[1]	Lehman, Müller, Munk, Senator, Zuntz.[2]	Luciani.[3]	Ajello and Solaro.[4]	O. & E. Freund.[5]	Cathcart.[6]	Benedict.[7]			van Hoogenhuyze and Verploegh.[8]	Brugsch and Hirsch.[9]	Howe, Mattill and Hawk.	
	Last food.	J. A.	Cetti.	Breithaupt.		Succi.		Beauté.	S.A.B. 73.	S.A.B. 75.	S.A.B. (Average).	Tosca.	Schenk.	E.	H.
1	22. 41	12.04	13.55	10.01	15.19	8.72	17.00	10.51	10.29	12.24	10.03	8.76	8.41	10.07	8.34
2		12.72	12.59	9.92	12.13	8.45	11.20	14.38	11.97	12.45	12.76	8.38	6.59	15.07	11.10
3		13.48	13.12	13.29	15.25	9.05	10.55	13.72	11.54	13.02	13.08	10.73	7.78	14.46	12.82
4		13.56	12.39	12.78	14.08	8.51	10.80	13.72	10.39	11.63	11.44	9.40	7.86	13.08	12.12
5		11.34	10.70	10.95	14.12	9.87	11.19	(11.30)	9.98	10.87	10.43	7.87	7.82	11.80	11.18
6		...	10.89	9.88	11.13	8.62	8.79	10.77	...	10.74	10.74	7.73	7.13	11.21	10.41
7		...	...	...	10.31	7.62	9.74	9.67	...	10.13	10.13	6.11	6.20	10.73	10.16

[1] *Skan. Archiv Physiol.*, **7**, 29 (1897).
[2] *Virchow's Archiv*, **131**, suppl. (1893).
[3] *Das Hungern*, *Leipzig* (1890).
[4] *La Riforma Medica*, **9**, 2, 542 (1893).
[5] *Wiener klin. Rundschau*, **15**, 69 and 91 (1901).
[6] *Biochem. Z.*, **6**, 109 (1907).
[7] Benedict, *Carnegie Pub.*, **77** (1907).
[8] *Z. physiol. Chem.*, **46**, 415 (1905–06), woman.
[9] *Z. exp. Path. Therap.*, **3**, 638 (1906), woman.

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variations in the total nitrogen excretion. The findings obtained from our experiment upon fasting men at moderate work show like changes to those already mentioned, there being an increase in the amount of nitrogen excreted on the second or third day and a gradual decrease to the end of the experiment. The excretion on the last day (seventh) of the fasts tended to approach a value very similar to that obtained by other investigators upon *men* (see Table VII, p. 589) *i. e.*, approximately *10 grams of nitrogen per day*. An interesting comparison may be made here with the findings from certain of Voit's experiments.[1] In these experiments he fed a 35 kg. dog with various diets having a wide nitrogen range and subjected the animal to a subsequent fast in each instance. His data indicate that the urea output for the seventh day was uniform no matter what the character of the diet which preceded the fast.

In our experiments the excretion of nitrogen after the first day was on a plane above that of the normal feeding period. This is a condition which did not exist in any of the experiments which have been heretofore reported. The explanation of this finding might at first thought be taken as an index of the effect of muscular work. However, upon comparison with the data of previous fasts and experiments reported in which muscular work has been a factor,[2] we are led to the belief that *this phenomenon was not due to the effect of work but rather was a result of fasting after a low-protein diet.* The preliminary diet of E contained 88 grams of protein, whereas that of H contained 76 grams. While these diets are not pronouncedly low-protein in character they are sufficiently low when considered in connection with the previous dietary history of these subjects to permit us to say that these men had been existing upon a low-protein diet for some time previous to the commencement of the fast.

We do not wish to be understood as claiming that the nitrogen level of the seventh fasting day was regulated in any marked degree by the fact that the subjects of our experiments came into the fast from a low-protein plane. The experiments of Voit, just referred to, would go to show that a similar level would have been reached upon this day even had the preliminary diet of these men contained 100 per cent. more nitrogen than that actually ingested. It is evident from a consideration of certain data obtained in this laboratory[3] that the claim of Voit does not always hold in the case of the dog. For example, in the investigation cited, the nitrogen excretion of the dog upon the seventh day of one fast was 2.56 grams whereas the nitrogen excretion of a subsequent fast was 1.13 grams upon the seventh day. This lack of agreement is

[1] *Z. Biol.*, 2, 307 (1866).

[2] Frentzel, *Arch. ges. Physiol.*, 68, 212 (1897); Lusk, *Science of Nutrition*, 2nd Ed., 79; Luciani, *Das Hungern*, (1890); Pettenkofer and Voit, *Z. Biol.*, 2, 459 (1866).

[3] Howe and Hawk, *Loc. cit.*

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all the more remarkable when it is recalled that the dog in question was in each instance brought into nitrogen equilibrium previous to the fast through the feeding of the same uniform diet. This lowered nitrogen output of the second fast we have interpreted as *indicating an immunity or resistance acquired as a result of the first fast* which permitted the animal to make a more economical utilization of its reserves when again subjected to the complete withdrawal of food.

Subject H showed a slight positive nitrogen balance during the preliminary period, an average of 0.331 gram of nitrogen per day, and Subject E showed a somewhat larger positive balance, an average of 1.480 grams per day. While the subjects maintained their body weights upon the low-protein diets and were in good health, they did not give evidence of having any marked fat deposits. The previous dietary condition of the subjects may, then, be offered as the explanation of the nitrogen excretion which during the fast was above the plane assumed during preliminary feeding. In other words, the two men possessed a minimum storage of fat and glycogen, two factors which permitted an early consumption of the readily available protein substances of the body.

Urea Nitrogen.—During the fast the urea nitrogen fluctuated both absolutely and relatively with the variations in the total nitrogen excretions. The relative urea-nitrogen excretion rose with the increased total nitrogen excretion and fell with the decrease in the latter. This was to be expected,[1] but in addition there was a gradual decrease in the percentage of urea nitrogen excreted as the fast progressed, which is common to the urea excretion for fasting men as has been shown by previous investigators.[2] This is brought out in a very striking manner in our experiments when it is considered that *the nitrogen excretion during the fast remained above, while the urea percentage after the third day fell below*, the level of that of the preliminary feeding period. The decrease in the urea output has been explained from the standpoint of acidosis.[3] As a result of feeding, the normal conditions were again resumed and the relative urea-nitrogen excretion tended toward that of the preliminary period.

Ammonia Nitrogen.—The ammonia-nitrogen excretion increased both absolutely and relatively throughout the fasts. The relative increase in ammonia corresponded to the decreasing relative urea-nitrogen output and is explained in the same manner, *i. e.*, as due to the condition of acidosis which resulted from fasting. In the case of the subjects of this experiment, acetone and diacetic acid were found to be present in the urine during the final days of the fast, the acidosis according to

[1] Folin, *Am. J. Physiol.*, 13, 66 (1905).
[2] Cathcart, *Loc. cit.*; Brugsch, *Loc. cit.*; E. and O. Freund, *Loc. cit.*
[3] Bonniger and Mohr, *Loc. cit.*

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qualitative tests being rather more pronounced in the case of H than in that of E. A consideration of the ammonia data will also show the output of ammonia to have been higher for H than for E during this period. This acidosis is believed to have been brought about through the formation of an excess of certain organic acids through the abnormal metabolic régime of fasting, the acids thus formed being ultimately neutralized by a portion of the ammonia which would in the natural course of events have passed by way of the portal circulation to the liver and assisted in the formation of urea. Instead of fulfilling this normal function, however, under the influence of the pronounced acidosis which accompanied fasting a certain portion of this ammonia combined with the organic acids and was eliminated from the body by way of the kidneys. Acidosis, therefore, was accompanied by an increased output of ammonia and a decreased urea excretion.

The ammonia-nitrogen excretion during the feeding period presented a peculiar phenomenon. We refer to the *marked increase in the ammonia output upon the third day*. This increase in the case of E was one of over 60 per cent., whereas in the case of H it was practically a 100 per cent. increase. There was a decreased output of urea in each instance but this decrease in the case of E fell far short of compensating for the high ammonia elimination. There was an accompanying increase in the output of creatinine.

A consideration of the data upon the percentage output of urea, ammonia and creatinine during the third and fourth days of feeding brought out a very striking condition in the metabolic processes of both subjects. Upon the third day occurred the high ammonia excretion and an increase in the quantity of creatinine excreted, while upon the following or fourth day of feeding, the nitrogen partition was very close to that of the preliminary feeding period denoting a return to the normal conditions of metabolism upon this day. It appears, then, that for a period of three days after the fast the metabolic processes were more or less in a chaotic condition due to the fact that the tissues were striving strenuously to make good the devastations brought about by the previous withdrawal of food. The anabolic processes were, therefore, stimulated far beyond the normal limits and all the varied activities of the organism were pushing forward the regeneration of the tissues and organs with the greatest acceleration. Through the very efficient coördination of the various functions of these two organisms, coupled with the further fact that a large quantity of food material was passed into them immediately after the fast ended, the activities which were making for a rapid regeneration were greatly aided. In a rough way we may consider that the normal rhythm of the metabolic functions was reassumed by the end of the third day. We are borne out in this assertion by the fact that the data ob-

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tained from an examination of the urine of the fourth day were approximately such as were secured from the normal metabolism of these individuals.

The excessive output of ammonia upon the third day was perhaps due to an attempt on the part of the organism to bring all the different phases of its metabolism to an approximately normal plane at the same time and for this reason all traces of acidosis were eliminated in the final effort. This process resulted in a much more pronounced ammonia excretion than had been in evidence during the two previous days. However, we cannot consider this very high ammonia excretion of the third day as due entirely to acidosis inasmuch as there was not a corresponding drop in the output of urea. This phenomenon may, perhaps, be explained upon the supposition that the acidoses of the previous days were somewhat more pronounced than the data indicate due to the fact that the ammonium compounds were not excreted as rapidly as formed during that period. This accumulation of ammonium compounds of various sorts may then be considered to have been retained in the body and excreted *in toto* upon the third day. This explanation seems the most logical for a condition such as we have here, *i. e., a very high ammonia excretion unaccompanied by an increased total nitrogen output or a compensating decrease in the urea excretion.*

As further evidence in favor of the belief that the plane of normal metabolism for these men had been reached by the fourth day we would cite the further facts that the creatinine coefficient was practically normal at this time and furthermore the subjects had regained at least 85 per cent. of the weight lost during the seven days of fasting.

If we examin the data presented by Cathcart[1] upon the professional faster, Beauté, we will note a similar attempt on the part of his subject to return to the plane of normal metabolism upon the fourth day of the feeding period subsequent to the fast. Our subjects, however, returned much more nearly to the normal plane than did Carthcart's subject. Carthcart makes no point of the fact that the metabolic régime of his subject came very near that of the normal at this time. In fact, he had no grounds for making an interpretation of this sort, inasmuch as just at this time he changed the diet of his subject from starch and cream to eggs and milk. It may be asserted that the change in diet was responsible for the pronounced alteration in the metabolic relations. In our experiments, however, there was no such change in the character of the diet and yet there was a very evident attempt on the part of the organism to assume normal relationships upon the fourth day.

The increased excretion of ammonia by Beauté upon the third day of the feeding period was not so pronounced as was this increase in the

[1] *Biochem. Z.*, 6, 109 (1907).

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case of E and H. However, the elimination was about three times as great as that excreted upon the following day or during the preliminary period. Furthermore, this was followed by a marked drop in the total nitrogen excretion with a return to a distribution of nitrogen very near the normal for this subject on the fourth day. A similar increased excretion of ammonia upon the fourth day of feeding has previously been reported from this laboratory[1] in connection with an experiment upon a dog subjected to "repeated" fasting.

It is a very interesting fact that the data from E and H and Beauté should be so very similar during the first part of the period of regeneration when it is appreciated that the diet in our experiment was a *high-protein* one, whereas, that of Beauté was practically *non-nitrogenous*. The data from Beauté if considered apart from the data on E and H might, perhaps, logically be interpreted as arising from the ingestion of a nitrogen-free diet, whereas the data from E and H if considered apart from Cathcart's report might be interpreted as brought about through the ingestion of a highly nitrogenized diet. Taking the two experiments under consideration, *i. e.*, Carthcart's and our own, we find that the main feature in common during the period in question was that the subjects in each instance were *ingesting food subsequent to a fast.* In one instance the food was *highly nitrogenous*, in the other it was *principally fat and carbohydrate.* However, the findings in the two cases, as already mentioned, were very similar *i. e.*, a very high ammonia excretion and low urea excretion upon the third day, followed by a return to conditions of nitrogen distribution closely approaching normal upon the fourth day. We would, therefore, give these findings a broad general interpretation and consider them as arising from the *ingestion of food by a fasting organism.* The character of the diet apparently had no very important bearing upon the situation.

Creatinine Nitrogen.—With the beginning of the fast, the creatinine-nitrogen excretion decreased slightly below the average of the feeding period and remained fairly constant at this new level throughout the fast with a slight tendency to decrease. Such a condition as we have described was to have been expected according to the ideas of Shaffer[2] and Folin[3] to the effect that the creatinine is an index of the muscular efficiency of the individual. The creatinine-nitrogen excretions in our experiment were nearly the same for the two men, denoting what was outwardly apparent, and equal muscular efficiency at the beginning of, and corresponding changes during, the fast. Relatively to the total nitrogen excretion, the creatinine-nitrogen excretion increased. Benedict[4]

[1] Howe and Hawk, THIS JOURNAL, 33, 215 (1911).
[2] *Am. J. Physiol.*, 16, 252 (1906).
[3] Folin, *Loc. cit.*
[4] *Loc. cit.*

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has presented data showing a decrease in the creatinine nitrogen as a result of fasting. His data also show an increasing creatine-nitrogen excretion such that he considers the total excretion of creatine plus creatinine as *practically constant* during a fast. In our own experiments in the case of E there was a *gradually decreasing* output of total creatinine (creatinine + creatine) after the second day, whereas in the case of H there was less regularity with a general tendency toward a decrease. Cathcart,[1] Benedict and Diefendorf[2] and van Hoogenhuyze and Verploegh[1] have also noted a gradual decrease in the creatinine excretion. Other experiments reported from this laboratory[3] have furnished further evidence that the creatinine excretion appears to be a function of the amount of active muscular tissue in the body.

Creatine Nitrogen.—There was a general tendency for the creatine-nitrogen excretion to increase gradually during the first part of the fast, this initial increase being followed by a decreased output. A marked exception to this gradual increase was observed in the case of E, who eliminated his maximum creatine output upon the *first day of fasting.* Benedict in his experiments noted, in general, a rise in the creatine excretion as the fast progressed. On the other hand, the data submitted by Cathcart show a rise and a fall in the creatine excretion during the first seven days of fasting after which the daily excretion remained fairly constant.

We have already mentioned the fact that the sum of the excreted creatine and creatinine was fairly constant for each subject for each day of the fast. There was, however, a tendency for this total to decrease slightly as the fast progressed, thus causing the average excretion for the first four days to be appreciably higher than the average for the last three days. In the case of H, these averages were 0.606 gram and 0.568 gram, respectively, whereas in the case of E the values were 0.630 gram and 0.566 gram. It is significant that the average daily total creatinine output for the final part of the fast was practically the same for each subject, *i. e.*, 0.566 gram as against 0.569 gram.

The total creatine-nitrogen excretion of E during the fast was 0.557 gram. If we consider this creatine as representing disintegrated muscular tissue we find by calculation[4] that it is equivalent to sufficient muscular tissue to liberate 20.06 grams of total nitrogen. As a matter of fact, however, the total nitrogen output for this period aggregated 86.436 grams for this subject. In other words, less than 25 per cent. of the total nitrogen output can be accounted for on the basis of the creatine eliminated.

[1] *Loc. cit.*

[2] *Am. J. Physiol.*, 18, 362 (1907).

[3] Howe and Hawk, *Loc. cit.*

[4] Fowler and Hawk, *Loc. cit.*; Howe and Hawk, *Loc. cit.*

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This condition was more pronounced in the case of H. The discrepancy becomes all the more evident when we recall certain other experiments made in this laboratory[1] which have demonstrated conclusively that the creatine content of muscle may be decreased 66 per cent. under the influence of fasting although retaining its nitrogen content but slightly decreased. It is evident, therefore, that a certain part of the creatine quota of the present study, which we have calculated as representing katabolized flesh, may logically be inferred as *having been removed from muscular tissue which was still functioning in the body* and which, therefore, aided in no way toward increasing the output of total nitrogen. Certain other experiments made in this laboratory have shown from an entirely different standpoint[2] that it is probably possible to remove creatine from muscular tissue without of necessity associating such removal with the katabolism of the creatine-bearing tissue.

The discrepancy mentioned as occurring between the total nitrogen output and the creatine output, considering for the moment that creatine represents disintegrated muscular tissue, might perhaps be partly explained on the basis that at least a portion of the excess of nitrogen arose from the katabolism of nitrogenous, non-creatinized substance within the organism. When katabolized, such constituents of tissue and fluids would aid in the augmentation of the total nitrogen output but would have no part in the creatine increase. One would expect, however, that the amount of nitrogen having this origin would be at the most a minimal quantity. It must also be borne in mind that the mere fact that the nitrogen content of fasting muscle is so near that of the normal is no absolute proof that muscle at some time, either before, during or after the removal of a portion of its creatine may not have lost a part of its nitrogen quota, a loss subsequently made good through synthetic processes.[3]

Summary.

Two men (instructors) of similar weight and general characteristics were fed for a period of seven days upon a uniform diet embracing a constant-water ration. Previous to this time they had been living upon low-protein diets for a period of at least six months, one upon a low-protein meat diet and the other upon a low-protein non-meat diet. After the preliminary feeding period they fasted seven days, receiving, however, a constant quantity of water each day. They meanwhile performed their usual college duties. Following the fast they were under observation for a period of eight days, during which time they ingested varying amounts of food without changing the quality of the diet as ingested in

[1] Howe and Hawk, *Loc. cit.*

[2] Fowler and Hawk, *Loc. cit.*

[3] Paton, *J. Physiol.*, 39, 485 (1910).

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the preliminary feeding period. The distribution of the urinary nitrogen, the changes in body weight, the alterations in the urine volume, including the relative percentage of the ingested water which was eliminated in the urine, were all carefully determined. The observations made upon the men in this experiment exhibited very uniform relative variations during the various phases of the study.

The withdrawal of food from these men was accompanied by the following findings:

1. An increase in the excretion of total nitrogen followed by a decrease.
2. A urea excretion which followed that of total nitrogen, although the percentage of the total nitrogen which appeared as urea decreased.
3. A small decrease in the quantity of creatinine excreted.
4. The excretion of creatine.
5. A fairly constant output of total creatinine (creatine + creatinine) for each subject for each day of the fast.
6. An acidosis. This acidosis was indicated by a marked increase in the ammonia output and the appearance of acetone and diacetic acid in the urine.
7. *With both subjects the excretion of total nitrogen during the fast remained above the plane of the normal preliminary feeding period,* with the exception of the first day of fasting. This unique finding we have interpreted as being due to the fact that the subjects *began the fast from a low-protein plane.* In spite of this unusual condition as regards nitrogen output, however, the nitrogen excretion on the seventh day was very close to that for the seventh day of fasting *men* as determined by other investigators, *i. e., ten grams.*
8. The largest water ingestion was *not* followed by the most complete elimination by the kidneys. A subject ingesting 1750 cc. per day eliminated 12–35 per cent. *less* than a subject ingesting only 1500 cc. per day.
9. A decrease in body weight, aggregating 7.44 per cent. for one subject and 7.62 per cent. for the other subject.
10. No discomfort with the exception of a slight feeling of hunger on the first or second day.

The ingestion of food by the subjects subsequent to the fast was accompanied by the following findings:

1. A marked retention of water during the first two days.
2. A pronounced retention of nitrogen from the second to the sixth day inclusive.
3. *A return to the normal metabolism upon the fourth day,* as indicated by the nitrogen partition. This return to the normal was preceded by an extremely excessive output of ammonia upon the third day. The return to the normal we have interpreted as having been brought about

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simply through the *ingestion of nutritive material*, the character of the diet having no important bearing.

4. It was necessary to place the subjects upon a higher nutritive plane after the fast than before the fast in order to maintain body weight and nitrogen equilibrium.

5. Contrary to the custom usually followed in "breaking" a fast our subjects ingested the *maximum amount of food* for any individual day upon the *second day after the fast.*

URBANA, ILL.

NOTES.

Note on the Determination of Halogens in Organic Compounds.—To Stefanov's method for the determination of halogens in organic compounds[1] which is based on the reducing action of nascent hydrogen, formed by the action of sodium on ethyl alcohol, Bacon[2] proposed a considerable modification in the procedure by which he uses the action of sodium ethylate on the halogen compounds. We tried this modified method using monobromobenzene and α-bromonaphthalene, both of which were carefully purified. For monobromobenzene the calculated percentage of bromine is 50.93. A Carius determination on the sample we used yielded 50.83 per cent. Br. With Bacon's method about forty trials were made, all of the results being low, and in no case were duplicates obtained which agreed, which showed that the reduction was incomplete and irregular. The results for α-bromonaphthalene were low also, but much nearer the calculated percentage. We thought that perhaps an increase in the amount of nascent hydrogen might effect a complete reduction, so $1^1/_2$, 2, $2^1/_2$ times the amounts of sodium and alcohol recommended by Bacon were used. The results obtained with monobromobenzene were 35.36, 50.96, 48.65, 49.19, 49.40, 47.43, 47.18 per cent. Br. It will be noticed that the second result is very near the theoretical, but we were unable to get a similar result again.

The sodium used was Merck's, and the alcohol 99.5 per cent.

In acidifying with nitric acid we noticed that if an excess were used a vigorous reaction occurred with the production of nitrous fumes, and the liquid was changed to a greenish yellow color, which persisted even if boiled. The compounds produced affected the end point in two ways, (1) the ferric thiocyanate seemed to become reduced, with the result that more potassium thiocyanate had to be added, thus lowering the result for bromine, (2) the end point was harder to judge. This difficulty, however, is easily eliminated by acidifying only slightly.

We are forced to conclude, therefore, that this method is not of general

[1] *Ber.*, 39, 4056 (1906).

[2] THIS JOURNAL, 31, 49 (1909).

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applicability, and especially cannot be used with difficultly reducible substances.

Since the above work was done, C. H. Maryott[1] published the results of his work on Stefanov's original method. His results appear similar to ours on Bacon's modified method. He found, however, that potassium gave good results. He did not try Bacon's modified method.

W. O. WALKER,
J. A. MCRAE.

SCHOOL OF MINING,
KINGSTON, ONTARIO, CANADA.

NEW BOOKS.

Physical Chemistry; its Bearing on Biology and Medicine. By JAMES C. PHILIP, M.A., Ph.D., D.Sc., Assistant Professor in the Department of Chemistry, Imperial College of Science and Technology. London: Longmans, Green & Co. 306 pp. Price, $2.10.

Since the appearance of Cohen's "Physical Chemistry for Physicians and Biologists" many advances have been made in the application of physical chemistry to biological problems, and a distinct need exists for a work which explains these applications, and the principles which underlie them, in terms intelligible to the ordinary medical student and student in biology. This need is very satisfactorily filled by the present work; the language is clear, and the experimental illustrations are well chosen.

No description is given, however, of the application of concentration cell measurements in the elucidation of biological problems, nor are the principles underlying the development of potential in concentration cells discussed. In view of the extensive applications which have been made of these principles in the past ten years in the investigation of such problems as the neutrality of the blood and the combining capacity of proteins for acids and bases, this omission is serious and robs the book of much of its usefulness.

On page 306 the discovery that the temperature coefficient of the conduction of a nervous impulse is of the same order as that found for chemical reaction velocities is attributed to Lucas[2] instead of to S. S. Maxwell.[3] T. BRAILSFORD ROBERTSON.

Essentials of Chemistry. By RUFUS PHILIPS WILLIAMS, Instructor in Chemistry in the English High School, Boston, Mass. 8vo. Cloth, 421 pages. Price, $1.25. Ginn & Co., Publishers.

In the preface the author points out 22 "innovations and departures * * * from current texts" which "are believed to be especially desirable features of the present book." Many teachers will feel inclined

[1] *Chem. News*, Jan. 6, 1911; *Am. J. Sci.*, 30, 378 (1910).
[2] *J. Physiol.*, 37, 112 (1908).
[3] *J. Biol. Chem.*, 3, 359 (1907).

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to take issue with the author relative to some of these "desirable features," however, especially when he speaks of "Preparation, Properties and Tests" being "the really essential matters" while "History, Occurrence and Uses" may be omitted by classes limited for time. The average student is not going to be a chemist, neither will he in his daily routine make tests; but the *humanistic* side of chemistry showing how man has learned to utilize substances for his welfare and comfort is of greater interest and probably of as great value to the educated man in the community as anything in chemistry.

The present book attempts to modernize an earlier work, but the spirit has not changed. This is evidenced by the fact that the main discussion of atoms and molecules is still introduced in the first chapter. The treatment of catalysis (page 46), hydrolysis (page 292) and the explanation of the alkaline reaction of sodium carbonate (page 140) accord better with the teaching of twenty years ago than of to-day. Several questionable statements and errors are found. The style is interesting and pleasing; the treatment of industrial topics is wide-awake. The book contains a great many facts of interest and value, but it is not clear that the student will gain an understanding knowledge of chemical principles and their application to life.

W. C. MORGAN.

Leitfaden der graphischen Chemie: Erläuterung einiger wichtiger Schulbeispiele mit fünf zusammenlegbaren Raummodellen. R. KREMANN, a. o., Professor der allgem. u. physik. Chemie an der Universität Graz. Verlag von Gebrüder Borntraeger, Berlin, 6 M. 60 Pfg.

The advantages of graphical representations, or at least of graphs combined with tables, over lengthy written descriptions is very marked, even in such simple cases as the pressure-temperature diagram for a one-component system and the melting-point diagram for a two-component system. These familiar diagrams are beginning to appear in chemical books of reference, and a knowledge of them will soon be indispensable for a chemist. In more complex systems, graphical methods of representation are, of course, still more important, but here the chemist is confronted with the serious difficulty of visualizing a three-dimensional figure. With the aid of space models this difficulty can easily be overcome, but sufficient time must be taken to examin in several cases the relation between the space model and its projections in different planes. Such individual work is now greatly facilitated by the simple and novel cardboard models designed by Kremann.

The five models, when enclosed with the 36-page explanatory note in a folding cover, occupy a space only two centimeters in thickness. Each of them consists of several pieces of cardboard securely fastened together in such a way that, by folding, and tying strings, the flat model may be quickly transformed into the space model. Each model represents a

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definit heterogeneous equilibrium, and is constructed to scale to correspond as closely as possible to the experimental data given in tables in the text. The quantities plotted along each coördinate axis are clearly marked, and the projections are printed on the two axial planes which form the basis of a model. The significance of each area is also given, and the connection between the spacial figure and the projections is emphasized by the use of the same letters with different subscripts.

The following examples of heterogeneous equilibria are considered: I. The two-component system, silver nitrate + water. The two axial planes represent temperature-vapor pressure, and temperature-composition of the liquid phase. II. The three-component system, potassium sulphate + magnesium sulfate + water. Each axial plane represents temperature and the concentration of one of the salts in the liquid phase. III. The three-component system, lead + tin + bismuth. Temperature is represented by the vertical axis, and composition is plotted in the horizontal plane in the well known symmetrical triangular diagram. The projections on the horizontal plane and on the vertical tin — bismuth — temperature plane are also shown. IV. The four-component system, ammonium nitrate + ethyl alcohol + methyl alcohol + water. The compositions are represented by means of a symmetrical tetrahedron. The projection on the ammonium nitrate — ethyl alcohol — methyl alcohol plane, and that on a plane parallel to both the methyl alcohol — ethyl alcohol axis and the water — ammonium nitrate axis are shown on another sheet of cardboard. V. The four-component system, water + the four salts, sodium chloride, ammonium acid carbonate, ammonium chloride and ammonium acid carbonate: a reciprocal salt pair. The model in position represents an inverted pyramid, whose horizontal cross section is a square; the projections on the horizontal plane and on a vertical plane parallel to one of the diagonals of the square are given. In the final chapter of the text, Jänecke's method of representing a reciprocal salt pair is illustrated by means of the example, water + the four salts, potassium chloride, magnesium sulfate, potassium sulfate and magnesium chloride.

WILLIAM C. BRAY.

Die Brown'sche Bewegung und die wahre Existenz der Moleküle. VON PROF. DR. J. PERRIN, Paris. (Deutsch von Dr. J. Donau, Graz.) Sonderausgabe aus Kolloidchemische Beihefte. Monographien zur reinen und angewandten Kolloidchemie. Herausgegeben von Dr. Wolfgang Ostwald. Dresden 1910, Verlag von Theodor Steinkopff, pp. 84. Price M. 2.50.

In this monograph of 84 pages, Professor Perrin presents an account of his interesting investigation of the Brownian movement as exhibited by colloidal suspensions of gamboge and of mastic in water. The lucidity and attractiveness of the author's style have been well preserved in the translation and the reader's attention and interest are held throughout

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with a power not usually displayed in scientific literature of this character.

The contents of the volume are divided into four parts. Part I deals with the description and history of the Brownian movement and its relation to the Second Law of thermodynamics. This is followed by an interpretation of the phenomenon in the light of the kinetic theory and an outline of the methods by which a study of the phenomenon leads (1) to a demonstration of the correctness of the fundamental postulates underlying the kinetic theory and (2) to a determination of the numerical value of Avogadro's constant, N, the number of molecules in one gram-molecular weight of any gas.

In his use of the term *osmotic pressure*, on pages 21 and 22, the author follows the almost universal practice of employing this term indiscriminately to denote two quite distinct quantities, (*a*) the *thermal pressure* of the solute molecules, and (*b*) the *osmotic pressure* properly so-called. This general practice is largely responsible for much of the confusion which exists in many quarters regarding the concept of osmotic pressure and its importance in our solution theory. The first of these quantities, the thermal pressure of the solute molecules, is the pressure corresponding to their mean translatory kinetic energy. For a sufficiently dilute solution, it is equal to two-thirds of the mean translatory kinetic energy per unit volume. The second quantity, the osmotic pressure, is the difference in the external pressures which must be applied to a solution and to the pure liquid solvent respectively, in order to produce equality in the vapor pressures (or in more general terms, the activities or thermodynamic potentials) of the solvent from each. This is a definit physical quantity, capable of direct measurement and connected with the freezing point, boiling point, vapor pressure, etc., by purely thermodynamic relations.

The thermal pressure and the osmotic pressure resemble each other superficially in that as the solution approaches infinit dilution they both approach the limit expressed by the familiar equation $PV = NRT$. As the solution becomes infinitly concentrated, however, the thermal pressure approaches the finite limit which corresponds to the mean translatory kinetic energy possessed by the solute molecules in the pure liquid solute, while the osmotic pressure increases without limit as the composition of the solution approaches the pure liquid solute. It is obviously with the first of these quantities, the thermal pressure, that Professor Perrin's experiments are directly concerned. The solutions with which he worked, were, however, so extremely dilute that their thermal and osmotic pressures were numerically identical.

In Part II, a kinetic equation is derived for the distribution of the particles of a uniform colloidal suspension under the influence of gravity. In order to calculate N from this equation, determinations of the volume

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and density of the spherical colloidal particles and measurements of the number of particles in a cross section at different levels are necessary. The remainder of Part II deals with the description of the experimental methods employed in these measurements and the results obtained. Prof. Perrin considers $70.5.10^{22}$ as the most reliable value for N. This corresponds to $4.11.10^{-10}$ c. g. s. electrostatic units, for the value of the elementary electrical charge, while Millikan's most recent value for this constant is $4.9016.10^{-10}$. The cause of this discrepancy has not yet been discovered.

Part III is the description of an experimental test of Einstein's formulas for the mean translatory and rotatory displacements of a molecule in a given time. The experiments show that a change of 100,000-fold in the mass of a colloidal particle is without an appreciable effect upon its mean translatory kinetic energy. The largest particles studied correspond to a solute with a molecular weight of 200 billion. One of the basic postulates of the kinetic theory, namely, the assumption that the mean kinetic energy of a molecule is independent of its mass and dependent only upon the temperature seems therefore to have received experimental confirmation *for a range of mass from that of the electron to that of a colloidal particle several hundred trillion times as heavy.*

Part IV comprises a brief survey and comparison of the various methods which may be employed to obtain the value of N. The monograph closes with a table of the values given by each method. The striking agreement among so many methods of such widely different character forces the reader to agree with the author's conclusion that the actual existence of atoms and molecules must be regarded as conclusively proved.

As one result of this conclusive evidence we may expect to see a radical change in some of our pedagogical methods in the next few years. Following the lead of Ostwald, it has been the custom with many authors of text books of general and physical chemistry to avoid, as far as possible, the use of the atomic theory and kinetic hypothesis in the presentation of the laws and principles of chemistry. The reasons for this method of presentation no longer exist. The kinetic and atomic principles should, in the future, serve as the *starting point* for the development of the laws of chemistry instead of merely the *hypothetical explanations* of these laws.

E. W. WASHBURN.

The Mineralogy of Arizona. By F. N. GUILD. Professor of Chemistry and Mineralogy, University of Arizona. 1910. The Chemical Publishing Co. 103 pp. Price, $1.00.

This small book aims to give "a fairly complete description of Arizona's minerals with some reference to their mode of occurrence, associations and chemical composition." The very general descriptions have been largely compiled from the literature, to which references are freely given, though the value of such a one as "Dana: Text-Book," may be in doubt.

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Typographical errors are not scarce: "United Geological Survey" (p. 14); "Tuscon" (p. 15); "according to informations furnished him" (p. 17); "Moisson" (p. 22); "U. G. S." (p. 26); "$(Pb,Cu_2)_3S.Sb_2S_3$" (p. 30) instead of $3(Pb,Cu_2)S.Sb_2S_3$; "Chrysophase" (p. 40); "Limonite, $Fe_2O_33H_2O$" (p. 45); "loboradorite" (p. 57); "Caronado mine" (p. 76); etc. Mineral names (in the body of the text) are capitalized in some places and not in others. Copper stained chalcedony, known by the trade name of "blue chrysoprase" is erroneously called chrysoprase (p. 40); dumortierite was not analyzed by Diller as stated on p. 67; copiapite is not an "unusually rare" mineral (p. 90); limestone, marble, caliche, graphitic clay and cement clay are included in this "Mineralogy." Some of the descriptions concern minerals from Mexico and an analysis of descloizite from the Argentine Republic is given (p. 77). A description of the method of analysis of this mineral covers more than a page. The accounts of the meteorites, of the various forms of silica, of the ice caves and of the caliche or calcareous deposits are much more interesting than the remaining paragraphs. While the book may be of value to those desiring a very general knowledge of the mineralogy of Arizona, it seems to the reviewer that with a little more effort and care, a book could have been produced that would have been far more creditable both to the author and to Arizona.

WALDEMAR T. SCHALLER.

Mineralogie de la France et de ses Colonies. Volume 3, Part 2 (1909), Volume 4, Parts 1 and 2 (1910). A. LACROIX. Librarie Polytechnique, Ch. Beranger, Editeur, Rue des Saints-Peres, 15, Paris. Price, Vols. 1–3, 30 francs each; Vol. 4, 35 francs.

This monumental description of French minerals, the first part of which appeared in 1893, is now completed, the publication of the last parts being delayed by the author's studies of vulcanism. The second part of volume 3 deals largely with the carbonates, of which calcite naturally takes the largest share, extending over about 170 pages and illustrated by 267 crystal drawings and photographs. Then follow descriptions, replete with crystal drawings, of the other rhombohedral carbonates. The descriptions of aragonite and azurite are very full and richly illustrated. Ctypeite is still regarded as a third modification of $CaCO_3$.

The first part of the fourth volume starts in with the manganites and plumbites. Psilomelane is described under the formula $xRO.yMnO_2.zH_2O$, of which the cobalt-bearing variety, asbolite, has an important economic value as a cobalt ore. Rancieite is a calcium-bearing variety of psilomelane. Then follow descriptions of the anhydrous sulfates and chromates; mascagnite, thenardite and metathenardite, which is the name given to a polymorphic form of Na_2SO_4, stable above 235° and differing in its crystallin and optical properties from thenardite. It was found at a secondary fumarole (temp. 500–590°) of Mt. Pélee and had evidently formed from

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fusion. There are then described glauberite, anhydrite, the barite group with many photographs and crystal drawings, the alunite group in which an occurrence of natroalunite from Martinique may be noted, and the rare compound lead and copper sulfates. The list of hydrous sulfates is an extensive one and includes mirabilite, gypsum (nearly 50 pages) and most of the vitriols. The rarer complex sulfates form an extensive list. Of the molybdates and tungstates there are wulfenite, scheelite and the wolframite group. Molybdite from Corsica showed qualitatively the presence of iron and water. The aluminates, ferrites, and chromites comprise the spinel group, the various members of which are fully described and illustrated. Only three borates are given, hambergite and rhodizite from Madagascar, and ulexite.

The second part of the fourth volume takes up the phosphates and related salts, the niobates and tantalates, and the organic mineral substances, such as the hydrocarbons, fossil resins and coals. The latter half is a supplement containing the new data on all French minerals. Of particular interest may be mentioned the various manganese phosphates and the full descriptions, with many illustrations, of the French phosphorites. The phosphorites are composed of minerals of great interest, economically as well as scientifically. These minerals are the amorphous colophanite, $x(Ca_3(PO_4)_2$ or $x(CaF)_2Ca_8(PO_4)_6 + yCaCO_3 + zH_2O$; the hexagonal dahllite $2Ca_3(PO_4)_2.CaCO_3 + {}^1/_2H_2O$ (see, however, *Am. J. Sci.*, (4th ser.) **30**, 309 (1910)); francolite, $(CaF)_2Ca_8(PO_4)_6.CaCO_3 + H_2O$, of which the fibrous variety is called staffelite and an unidentified fourth mineral, differing optically from dahllite and francolite but similar to them in chemical composition. Quercyite is the name given to those phosphorites which consist of the amorphous colophanite and one or more of the other three minerals just mentioned. If only dahllite and francolite (both optically negative) are present, we have α-quercyite; if the fourth unidentified mineral (optically positive) is also present, we have β-quercyite. A number of new mineral names are introduced in this volume and the entire work, in four volumes, is a lasting tribute to both the author and to France. It is an indispensable mineralogical reference work of the highest order. WALDEMAR T. SCHALLER.

Municipal Chemistry. A series of thirty lectures by experts on the Application of the Principles of Chemistry to the City, delivered at the College of the City of New York, 1910. Edited by CHARLES BASKERVILLE, PH.D., F.C.S., Professor of Chemistry and Director of the Laboratory, College of the City of New York. New York and London: McGraw-Hill Book Company. 1911. pp. ix + 526. Price, $5.00 net.

The thirty chapters comprising this volume present the substance of an equal number of public lectures on topics relating to the welfare of urban communities from the standpoint of chemistry applied to munici-

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pal affairs. The topics treated by the eighteen lecturers include the Sanitation of the City (Baskerville), Drinking Water Supplies and Their Purification (Mason, Flinn), Milk (Darlington), Food Adulteration and Inspection (Wiley, Hamor), Drugs and Their Adulteration (Coblentz, Kebler), The Construction and Sanitation of Streets and Roads (Cushman, Edwards, Very), The Disposal of Wastes and Sewage (Very, Winslow), The Making and Valuation of Illuminating Gas (Elliott), the Smoke Problem (Parsons), Ventilation (Moody), Personal Hygiene (Storey), Textils (Olney), Combustibles and Explosives (Breneman), Paints, Metal Corrosion, Cement and Concrete (Toch), and Parks and Playgrounds (Britton).

The editor, in his preface, presents an earnest appeal for an increase of intelligent and aggressive interest in municipal affairs, which is quite in harmony with the subject matter of this series of lectures. The topics are, in general, treated in a way to reach the reader who has no accurate scientific knowledge and to appeal to his common sense and his civic pride; and chemists who are not closely in touch with this field of work can hardly fail to find much of interest in these pages. This is particularly true of the teacher who desires to utilize the applications of chemistry to affairs of everyday life in order to enforce his instruction in the principles of the science. A few of the chapters, notably those on the New York water supply, on the detection of adulteration in drugs, corrosion of metals, cements and concretes, and textils are necessarily more technical than those on general questions of sanitation, or food and water supplies, and in some of the former, especially that on textils, the writers seem to have wandered rather far afield from the general topic, to the probable discouragement of the layman to whom the rest of the book will appeal. An elaborate index makes reference to special topics an easy matter.

As an example of the publisher's art this volume falls so far short as to call for unfavorable comment. The print is not clear on many of the pages, there are many imperfect letters and in at least two instances (pp. 122 and 327) entire lines have been misplaced. The paper (at least in the copy submitted for review) has been badly soiled in passing through the press and shows imperfections of structure. The cuts have in many cases not been fortunately chosen and in many more they are badly blurred in reproduction. For the price demanded, a more finished volume could well have been supplied.

Although these mechanical imperfections somewhat mar the reader's enjoyment of the book, it will still be found to be a most interesting collection of monographs upon timely subjects and should serve an excellent purpose in directing public attention to municipal needs and

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individual duty, and to emphasize the vital importance of the service which chemistry and its followers can render for the public weal.

H. P. TALBOT.

Das Oedem—Eine experimentelle und theoretische Untersuchung der Physiologie und Pathologie der Wasserbindung im Organismus. DR. MARTIN H. FISCHER, Professor of Physiology in the University of Cincinnati. In deutscher Sprache herausgegeben von Karl Schorr und Wolfg. Ostwald. Dresden, 1910. Verlag von Theodor Steinkopff. Pp. 223. Price, 6 M.

This monograph is described in an introductory chapter by Dr. Wolfgang Ostwald as representing the most important advance in the solution of one of the fundamental problems of general biology and pathology that has been experienced since the application of the theory of osmosis. For the chemist the primary interest in the book lies in the rather ingenious attempt to explain a series of physiological and especially pathological phenomena on the basis of the behavior of colloids. After an introductory consideration of these somewhat indefinit states of matter from the standpoint of modern physical chemistry, the author reviews his experimental studies of the conditions under which the swelling of fibrin and gelatin—a typical colloid phenomenon—takes place. He proceeds to compare this with the retention of water in the colloid (protoplasmic) structures of which tissues are built. Changes in the reaction of the medium, *e. g.*, the development of acidity, may suffice to alter greatly the "affinity" of the tissue for water. The antagonistic influence of various anions and cations in this change is illustrated. The author critically reviews the earlier theories which postulated variations in blood pressure, dilution of the blood, etc., as the essential factors in the causation of oedemas. He maintains that the phenomenon must be associated primarily with the tissues themselves. Local changes such as, for example, the development of acid incident to oxygen starvation, may make possible the retention of water in the colloid tissue structures in the manner already indicated. Thus, also, the (acid) sting of insects induces a local edema of the skin. Further specific illustrations are developed in detail.

One must admit that the application of theory to actual biological conditions is in places rather overdrawn; and it is more than doubtful if any single group of factors can account for all the phenomena discussed. The treatment is in harmony with the current interest in the chemistry of the colloids. The book is suggestive, even if not everywhere convincing; and it will appeal to any one interested in this trend of biochemical investigation. In its original English form the monograph was awarded the Hatfield prize of the College of Physicians in Philadelphia, in 1909.

LAFAYETTE B. MENDEL.

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RECENT PUBLICATIONS.

BASKERVILLE, C., AND ESTABROOK, W. L.: Progressive Problems in General Chemistry. Boston: Heath. 12°, 243 pp., $0.90.

BECK, K., AND STEGMÜLLER, P.: Ueber die Löslichkeit von Bleisulfat und Bleichromat für sich, in Gemischen und in Form von Oelfarben in verdünnter Salzsäure sowie über das Gleichgewicht von Chromat und Bichromat in Lösung. Berlin: J. Springer. 8°, 2.40 M.

BENNECKE, A.: Beitrage zur Mutterkornforschung. Rostock: H. Warkentien. 8°, 1 M.

BERTRAM, J.: Ueber Kondensationsprodukte des Alloxans und seiner Homologen mit Benzoylessigsäureestern. Berlin: Emil Ebering. 8°, 1.30 M.

BLÜCHER, H.: Auskunftsbuch fur die chemische Industrie. Berlin: F. Siemenroth. 7 Aufl. 15 M.

BUHL, T.: Maschinen und Materialien im allgemeinen Fabrikbetrieb. Tübingen: S. Weil. 3 M.

CURIE, P.: Traité de radioactivité. 2 Vol. Paris: Gauthier-Villars. 8°, 30 Fr.

DEJONGHE, G.: Technologie sucrière. Paris: Dunod & Pinat. 8°, 15 Fr.

DODONOW, J.: Ueber die Spaltung des racemischen Kairolinoxyds in optish aktive Komponenten. Berlin: Emil Ebering. 8°, 1.50 M.

ESCARD, J.: Les substances isolantes et les méthodes d'isolement. Paris: Gauthier-Villars. 8°, 10 Fr.

FIEDLER, A.: Synthese von Polypeptiden-derivaten der Asparaginsäure. Berlin: Emil Ebering. 8°, 75 Pf.

FRAENKEL, S.: Dynamische Biochemie; Physik und Chemie der Lebensvorgänge. Wiesbaden: J. F. Bergmann. 16 M.

FRIEDLÄNDER, P.: Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige. 9 Teil 1908-1910. Berlin: J. Springer. 8°, 64 M.

FUHRMANN, F.: Der Oeldruck. W. Knapp. 2.80 M.

GALATES, L.: Abbau des Laudanosins. Berlin: Emil Ebering. 8°, 1.30 M.

GROSS, C.: Studien über Biphenylensulfamin. Berlin: Emil Ebering. 8°, 1 M.

HAEDER, H.: Die Dampfkessel. 5 Aufl., 2 Teil. Wiesbaden: O. Haeder. 8°, 5.50 M.

HAENIG, A.: Der Erz-und Metallmarkt. Stuttgart: F. Enke. 8°, 10.80 M.

Handbuch für die internationale Petroleum-Industrie 1911. Berlin: Finanzverlag. 10 M.

HARTWICH, C.: Die menschlichen Genussmittel. 10 Lfg. Leipzig: C. H. Tauchnitz. 2 M.

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EDUCATIONAL SUPPLEMENT

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THE EFFICIENCY OF COLLEGE TRAINING OF MEN FOR THE CHEMICAL INDUSTRIES.

BY CHARLES F. BURGESS.

An estimate of the efficiency of college training of men for the chemical industries must necessarily be based upon the qualifications which the men possess during the first years immediately following their college course, and not upon the work done either by undergraduate or graduate students.

According to observations of the writer, fully 90 per cent. of college graduates who enter the industrial chemical field make their beginning in analytical chemistry, and of these men an even greater percentage are ambitious to get beyond this stage into the works where they may have charge of productive operations.

As a typical example of the graduate who achieves success, let us follow one for a few years after graduation. His career began with an appointment as chemist in the analytical laboratory of one of the branches of a large chemical industry operating a number of plants throughout the country.

On a salary of $12 per week, and his bare living expenses being thereby assured, he gave his undivided attention to the chemical work constituting his assignment. This consisted of sulfur determinations in each of a large number of samples of ore supplied daily to the laboratory. No freedom was allowed in the choice of methods, but he was given careful instruction in a method, new to him, which had been adopted as the standard of this department. As he grew proficient, he became weary of this task, but through constant repetition he found opportunity for reflection and observation. It was a revelation to contrast the number

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of analyses which could be made in a given time with the determinations obtained in like time in the college laboratory.

The head of the laboratory, who held the title chief chemist, was his instructor, and was far more insistent upon accuracy and despatch than had been any of his college instructors. He was evidently a man of long years of experience in analytical chemistry, who had acquired the knack of handling a laboratory force so that it could turn out analyses at a remarkably low cost per determination. Although college bred himself, he did not hold this to be an essential requirement for analysts, since he had taken young apprentices from the shop and offices and successfully trained them to perform their daily duties of analytical determinations with accuracy and speed.

As diversion from the daily routine grind, new materials were occasionally submitted for analysis, and these required the use of new methods and an examination of the very limited literature available in the laboratories. This new work was turned over to those of the laboratory force who had received college training, their results being checked carefully by the head chemist. Presently it was rumored that the accuracy of some of the analytical results turned out in the laboratory was being questioned at the head office, where a lack of agreement between figures obtained in the company's different laboratories had been detected. This resulted in an uneasy feeling until the arrival of a representative from headquarters known as the chemical auditor. He was a man of national reputation as an analytical chemist, the owner of a Ph.D. degree, and his duty consisted in gleaning the results of research work appearing in the chemical journals, in working out and standardizing methods best adapted to use in the branch laboratories, and in a general supervision of these analytical laboratories to insure that they were all working in harmony and coöperation. He began a careful inspection of the details of the methods employed in this laboratory, and soon found some causes for discrepancies.

His acquaintance with this noted authority gave our young student his first contact with a chemist whose position he envied, but his envy was tempered by the reflection that there were few positions of this rank and responsibility in the country, while a large army of analytical chemists were competing for them. This did not discourage him, however, but he had his moments of discontent. One of these came one day when he was seated at a balance, making a moisture determination. On one side of him sat a former office boy making an ash determination, and on the other a man recently taken from a labor gang was weighing an ore sample. An official of the company looked in upon them, commenting jocularly on the "three little chemists sitting in a row." Our young man saw the

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joke, but that night he wrote to his former friend and adviser, the Professor of chemistry of his Alma Mater, as follows:

I have been in this laboratory to which you recommended me for nearly a year, and have now come to the conclusion that it will be advisable to make a change. Can you advise me of an opening? All of the employees of this department are ranked on the pay-roll as chemists, though less than half of them have had any chemical training whatever before coming here. There seems to be no opportunity for advancement. The four other college graduates with whom I am working are likewise discouraged. Delay in promotion does not come from mediocre ability; the head of the laboratory is one of the ablest chemists I have known. He has been here for eleven years, and is now getting but $125 per month. I have had a good training in general and analytical chemistry, but even if I had spent my entire college course in the study of this branch, my opportunities would be no better than they are at present. All of the real thinking is done for us by a few men whom we seldom see.

"In contemplating the numerous uneducated men in the laboratory who are called chemists, I do not take as much pride in holding that same title as I had expected to while in college. It seems to me that if it were only possible to get into the works as assistant to a department superintendent, the chances for advancement would be greatly improved, but such opportunities are seldom presented.

All his old professor could say in encouragement was to assert that the majority of college graduates in chemistry get into analytical work as a stepping stone to something better; that in the analytical laboratory the employers practice a weeding-out operation, separating the men of ordinary ability from those possessing enterprise, persistence, resourcefulness, and other qualities contributary to success; that although this process is frequently a slow one to a man really deserving, promotion is bound to come; and that, therefore, he should not resign, but try to make himself so proficient that when an opportunity presented itself, he would be ready to make the most of it.

Not entirely convinced that his professor really understood the situation, the young man determined to prepare himself for opening the door for opportunity when it should knock. First he took up a general study of the manufacturing business in which the company was engaged—the economic factors which had determined the location of his branch at that particular point, such as labor conditions, transportation facilities, source of raw material supply; the costs of generating steam and power. He further studied the details of the manufacturing operations as far as he could get to them; the relation of the analytical laboratory to the works at large, etc.

He found that the library facilities were decidedly inadequate for this study, consisting of a few books and several scientific publications, and that none of his associates, not even the head chemist, was familiar with the works operations. They had no interest in their work after the re-

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sults had been recorded and sent to the office, and the significance of analyses upon the larger problems of the company did not concern them.

Thrown, therefore, upon his own resources, he made a survey of his college training, hoping to determin what portion of it might now be of assistance. Because of his meager salary, he could not afford to subscribe for the best scientific and technical publications, but he had learned that a large amount of useful literature was available for the asking, and so appealed to such agencies as the census bureau, various other government departments and laboratories, the state geological surveys, the bureau of labor and industrial statistics. Using what they sent him he resumed the course in economics which he had taken at college. He reviewed his work in steam engineering and power generation in the light of application to the conditions of his plant. His old work in mechanical drawing and machine design enabled him to produce working drawings of a labor- and time-saving laboratory device. Metallography had taught him the value of the microscope in the study of materials, and getting out the dust-covered microscopic equipment, he found he could determin quickly some of the properties of the materials which the slower chemical analyses were revealing. This study of costs of chemicals and other materials received and manufactured, not from laboratory supply lists but from wholesale quotations of trade publications, gave him an idea of opportunities for manufacturing profits. Out of such diversified lines of studies as these came a gently increasing interest in his routine work.

Finally opportunity knocked at his door, and he was placed in charge of the filter-press room, where a comparatively simple operation was kept going night and day. This consisted in treating a ground ore with a chemical solution yielding an insoluble, valueless filter cake and the valuable filtrate. This new foreman found that the principal item of cost was the renewal of filter cloths, amounting to a total of $1.50 per ton of ore treated, and he began a study of the possibilities of decreasing this item. The rapid wear on the cloths was due to the action of the solution on the fibers, and more especially to the wear on the upper edges of the plates where they were pulled apart for dumping. He satisfied himself by a study of the action of this chemical solution on various kinds of fibers that they were employing the best material. By subjecting the cloth in different directions to a strength-testing machine, he found that a stress elongation diagram was obtained which taken in one direction of the cloth was similar in shape to that for mild steel, and in the other direction to cast iron, as he had obtained these curves in his college testing laboratory. This yielded a method of drawing specifications for cloth best suited to the requirements, and resulted in some small reductions in cost, but not enough to be satisfactory. Since the wear

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was directly proportional to the time, and to the frequency of dumping the presses, it was evident that this could be reduced per ton of ore only by more rapid working, and by making a thicker filter cake. To this end the pressure of the feed was increased by changes in the pumping machinery. The principal hindrance to more rapid working was found to be the hard, flinty precipitate which formed on the plates and filled up the grooves. It was the custom to remove this coating by a pneumatic chipping hammer, requiring several hours of labor per plate. An attempt was then made to find a labor-saving solvent, but solubility tables gave our young man no assistance. Solvents which would dissolve this precipitate were either too costly, or would attack the iron as well as the scale. He discovered, however, that a caustic soda solution of certain strength, while not dissolving the scale, would in four days' time soften it so that it could be brushed off readily. A calculation of the interest and depreciation on investment in plates tied up while under this treatment showed the sum to be far less than the labor involved in the older method, which method was then discarded. The cleaner plates, higher pressures, and better cloths enabled the filter cake to be doubled in thickness in equal time, and the cost of cloths per ton of ore treated was reduced one-half, resulting in a daily saving of $50.00 in this one item alone.

With such a record of reducing cost, it naturally followed that our young man was given other opportunities to exercise his abilities. He was transferred to a branch plant, where sulfuric acid was being made by a newly developed contact or catalytic process. His problem now was to assist in the determination, if possible, of some way to prolong the life of the contact mass, upon the solving of which was dependent the commercial success and, therefore, the continuance of the use of the process.

In undertaking this problem, our protegé recalled his college thesis work, in which he had been trained in systematic procedure beginning with a statement of the problem, a summary of the state of knowledge based upon the literature and other sources of information, an outline of proposed experimentation, the execution of the work, the significance of the results in application to the problem in hand, and conclusions or recommendations based upon the investigation.

In applying this method to the new problem in hand, he found himself involved in work of a highly scientific order, comparable with the best of that done in university laboratories. He became as deeply interested in it, through an appreciation of its practical importance, as any pure scientist can become in his labors, even though appreciating that his results would not, on account of the company's policy of secrecy, be given out for publication.

Such is a narrative typical of the progress of a successful industrial chemist who benefits by his college training. The industrial people

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claim that the colleges are not doing all that is possible to fit men for industrial work. The educational chemists are divided in opinion as to what methods they should pursue in meeting these demands. The majority of them believe that more of a student's time should be devoted to chemistry; that they should turn out men more skilled in analyses, while others hold that it is no more the function of a university course to turn out skilled analysts than it is that of a mechanical engineering course to turn out skilled machinists or draughtsmen, or of an electrical engineering course to graduate proficient electricians. The recent introduction and present multiplication of courses in chemical engineering is in line with the views of the latter class of educators who are designing a course of study which will give to its graduates numerous viewpoints from which to regard chemical work; to acquaint them with the most useful tools for attacking industrial problems; and to qualify them not as skilled engineers or chemists upon graduation, but as men capable of learning and progressing after getting into industrial work, so that they may earn the title which is too frequently bestowed upon the graduate at commencement time.

Shall college training for chemists be intensified or diversified? Shall the training in chemistry be such as to entitle its possessor to call himself an analytical or organic, or metallurgical chemist upon graduation and limit him to pursuit in his already chosen field; or shall the training in chemistry be reduced in quantity and supplemented by study in allied subjects, so as to give a broader training, a greater versatility, and a wider range of opportunities for employment?

There are few teachers of chemistry who will deny that a broader scope of study is desirable, but there are equally few who will agree to any reduction in the amount of attention to their particular subjects. This is the basis of the growing sentiment favoring a five-year college course for industrial chemists. The writer is unable to see a solution of the problem through a lengthening of the course of study, and believes that if the fields of the technical applications of steam, electricity, hydraulics, mechanics, and the like, can be occupied successfully by men having four years of college work, there is no fundamental reason for requiring a longer course for men for industrial chemistry. The remedy for apparent crowding should come, therefore, through redesign or improvement of the four-year courses. One way of accomplishing this is through less intensification in purely chemical studies, and the time-consuming laboratory practice accompanying them. While proficiency in some particular lines might thus be sacrificed, the student could be given an interest in and knowledge of the basic principles of those lines which will enable him to continue his studies after graduation; and in

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the additional studies thus made room for, his total efficiency may be materially increased.

It is a fundamental error to introduce courses in industrial chemistry, or chemical manufacture, in the belief that they will give a man a working knowledge of the technical details of some particular manufacturing business which he may enter. Should a student know that he is going into the cement business, it would be time poorly spent in his college course to devote part of it to a study of technical details of cement manufacture. The manager of a large telephone company employing many college graduates each year specifies that he wishes men broadly trained rather than those who have spent time in studying the details of telephone practice, since instruction of the required kind can be given most efficiently while in the pay of the employer.

There are, however, other and good reasons for giving courses in industrial chemistry, and especially if they can be given in such manner as to increase a student's interest. The work should give him a general view of the field of technical chemistry, and of the interrelationship between the important chemical industries. It should give him the beginning of an appreciation of the commercial factors which are inevitably linked with the production of chemical materials. Such a course should teach how and where to find information as to chemical processes rather than aim to impart information about such processes. The books used should be reference rather than text-books. The student of chemistry usually finishes his course with but little appreciation of costs and values. The price lists with which he may have become familiar are those of the dealers in supplies for chemical laboratories. "The introduction of the dollar sign into the chemical equation," and the necessity of keeping the balance upon the right side of the equation, opens to the student an entirely new and a most interesting view of the field of chemistry. Frequent reference to lists of wholesale prices of chemicals such as are given in the *Oil, Paint, and Drug Reporter*, and other similar trade publications, with explanation of trade usages in making trade quotations, the influence of freight rates, the method of packing as influencing rates, import duties, insurance risks, and the like, may well constitute an important part of the teaching of technical chemistry.

The differences of opinion of the chemistry teachers and the industrial men on educational methods are due in large part to the attitude of the former toward industrial work. There is undoubtedly a tendency for the college chemist to regard his technical brother as one immersed in routine work and to whom chemistry has become a trade rather than a profession. A statement of significance in showing the attitude of the one class of chemists toward the other is taken from a presidential ad-

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dress which concerned the welfare of the American Chemical Society and the publication of its Journal:

Those engaged in industrial pursuits must always remember that although they equal in number the educators and other students, or may even form a majority of the society, it is none the less true that the former are, and no doubt will continue to be, the greater producers of new and original matters, and hence deserving of greater consideration in proportion to their numbers than those who are less productive.

Any one who has had an opportunity to review the new and original work being done in industrial fields cannot help but feel a profound admiration and respect for the high-grade research work which forms the basis and the immediate means of realization of much of the industrial progress on which the present age prides itself. While the writer does not assume authority to reply for all industrial chemists, he believes that if they were not restricted by commercial policies of secrecy, their publications of new and original scientific work would be just as numerous, and quite as valuable, as those of their unrestricted brothers in the educational laboratories. Investigation work carried out to meet industrial needs may be, and frequently is, as distinctly scientific as that which is done to fulfil the requirements of a doctor's thesis.

This attitude of chemistry teachers toward the industrial field is shown by the fact that a large majority of students taking advanced graduate work have done so in preparation for teaching positions. But that graduate work is not merely a means of getting into educational work is demonstrated by the large and increasing numbers in the graduate departments of our engineering schools, who are looking forward to industrial pursuits.

In conclusion, the writer asserts his belief that there is in general an inefficiency in the college training of men for industrial chemistry; that this training is largely in the hands of men who have an insufficient acquaintance with and appreciation of the requirements of the industrial workers; and that when educational chemists and industrial chemists finally come together on common ground, some of the present difficult educational problems will disappear.

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A LABORATORY COURSE OF CHEMICAL ENGINEERING.

BY WILLIAM H. WALKER AND WARREN K. LEWIS.

In order that the suggestions as to the make-up of a course of Chemical Engineering contained in this paper may be as concrete as possible, we have made a number of assumptions which it will be well to state at the outset. First, the work here outlined is intended to form a part of a *four*-year course such as is given in our engineering schools, and no attempt

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has been made to even discuss matter which should be taken up in a fifth year, however desirable such matter may be. Second, the course here presented is designed for that class of students that hopes upon graduation to be in position to accept employment in any line of chemical industry, rather than those who by becoming relatively expert in one industry are thereby limited to that particular field. Third, that students taking the course here outlined shall have had an adequate training in the fundamental subdivisions of chemistry, including descriptive industrial chemistry, and the essentials of physics, mechanics, and thermodynamics. Finally we make the assumption that the future employers of the men so trained are willing and, in fact, expect to teach these men the details of the particular work for which they are employed.

While we do not depreciate the good work of the trade schools, nor do we fail to recognize the opportunities open to the graduates of such schools, we believe that a training that devotes so large an amount of time in a four-year course to the details of the manufacture of one industry cannot produce the man to whom that industry must look for its final improvement and progress. The reason for this seems obvious; no school can teach much concerning soap making for example, which is not already known as a part of this art. Hence the very best that can be done is to turn out a soap maker who knows all that is now known about this particular industry. He has not obtained and cannot get in a four-year course, that sound general knowledge of the principles of chemistry in its broadest sense, or the fundamental concepts of engineering; he knows only those principles which are involved in soap making. But to solve the problems in soap making requires knowledge other than that already applied to this industry; were this not so these problems would have been solved long ago.

Hence we believe our last assumption to be a sound one, namely, that the employer should and must expect in taking on a new man fresh from an engineering school, to teach him the factory details of the work for which he is employed, in order that he may get a man with the breadth of knowledge necessary to his best interests. When such a man has learned the practice of soap making or tanning from capable foremen in the factory and is then brought face to face with the problems which exist there, he is able to climb into the conning tower as it were, take a survey over the entire field, and as a result bring to bear upon the solution of the problem, the principles of chemistry and engineering which, although possibly applied to other arts, are also applicable here. He does this in a way that an expert in that particular industry alone, but deficient in general scientific training, can never do.

It is but a truism to day that our chemical engineer should have adequate training in a laboratory of chemical engineering. Doctors

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of medicin have hospital clinics, mining engineers their laboratories, and why not then a laboratory of chemical engineering. But of what will it consist, and how will it attempt to teach the things the men most need to know?

The choice of suitable experiments for such a course may be aided by the consideration of a few general principles:

1. The student must be given some idea of the factors which enter into the economy of a process. Although he has had both organic and inorganic preparations this work was taken up from an entirely different point of view. He does not appreciate, for example, that boiling off water is expensive, or that a process may, on account of special conditions imposed, be more expensive to operate at a high chemical efficiency, than when the reaction is allowed to proceed at a lower efficiency. The study of a reaction for itself is the function of the laboratory of general organic or inorganic chemistry; the details of factory practice can best be learned in a factory; but an economic point of view can not be learned in the first, and should be acquired before the student enters the second.

2. The experiments selected should be those which typify some important fundamental principles, and in which these principles can be made to stand out in strong relief; there is always danger of covering up the principle with the details of an operation.

3. The experiment should be one that admits of theoretical discussion. One of the greatest difficulties that a teacher has is to get his students to use their knowledge of theoretical or general chemistry or physics in their engineering laboratory work. The more completely and accurately, therefore, that the results of variations in the conditions of an experiment can be predicted before the experiment is begun the more valuable it is. It is also desirable that these modifications or variations of conditions be involved in the plan of the experiment, in order that what may be called the "spirit of research," or thesis idea, may be introduced into the class work. That "research" should be rigorously delegated to special men in specially equipped laboratories is a basic error which can do much harm in educational work. While valuable results can, in general, be obtained by only more highly trained men working through consecutive hours for a considerable time, yet the spirit of investigation can be introduced into a great deal of our more advanced laboratory work. It is possible to divide the class into groups, and so plan the conditions of the experiment that each group will contribute, by the average of their individual results, to the solution of the problem as a whole.

4. And, possibly most important of all, the experiment must admit of reasonably accurate work. Nothing is more nearly fatal to laboratory success than to choose, as experiments, processes which cannot be held

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sufficiently under control to make concordant results possible from each member or group of members of the class.

The following series of experiments illustrate the kind of work which has been found instructive in the laboratory of the Massachusetts Institute of Technology and are offered here merely as suggestions.

1. One of us has published[1] in considerable detail a laboratory experiment on the electrolysis of brine which is well calculated to familiarize the student with the industrial significance of electricity when used as a chemical reagent. The relation of amperes, watts, coulombs, etc., to the cost of the resultant product is here brought out in a way that gives the student working grasp of these unit quantities obtained only in such a way as this.

2. Almost every industrial chemical laboratory will have a steam-jacketed kettle of some sort in its equipment but how much does a student usually gain from such a piece of apparatus? He makes in it, let us say, a batch of soap. The chances are that the product will be poor and the cost high; even under the instruction of an expert soap maker, he will learn, at best, only how soap is made. But his power to solve problems in chemical engineering has not thereby been increased.

With even so simple an apparatus, however, the principles of the application of heat to liquids may be well illustrated. Let the student measure the pressure of the steam and, by means of a throttling calorimeter, its quality as it enters the jacket and determin the amount used by weighing the condensed water. From these data he can calculate the total heat consumption of the apparatus. He can determin the amount of water evaporated at definit time intervals by measuring the increased concentration of the solution by either titration or specific gravity. He can thus obtain the heat consumption per pound of evaporation, determin the efficiency of evaporation and the heat losses. By using different solutions the variation of the heat of vaporization may be emphasized. He can determin the heating surface necessary for a given rate of evaporation and study the efficiency of lagging material. By substituting for the steam-jacketed kettle a barrel with a steam coil of known dimensions other variations may be introduced. Although the student may have worked with small and inefficient apparatus, he leaves the work with a vital grasp of the principles of the application of heat to liquids.

3. In connection with the previous experiment the uneconomical nature of open pan evaporation will be emphasized by the analysis of the heat losses. This leads to the problem of multiple-effect evaporation which is of such great and growing importance in chemical industry. If the laboratory of chemical engineering is to ape industrial conditions

[1] *Proceedings Electrochemical Society*, 9, 23.

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and show the student only the best practice in carrying out a given operation it should be equipped with a complete triple or quadruple effect evaporator. We would, however, advise against this installation. More efficient instruction can be given by use of a single-effect apparatus, designed to stand either pressure or vacuum, and fed with boiler steam through a reducing valve, capable of close regulation. The problem of the manufacture of caustic soda, involving as it does a nice cost balance between the expense incurred in concentrating weak caustic liquor and the incompleteness with which the causticizing reaction may be effected in a concentrated solution, is well adapted to this work. A run is first made using the highest feasible steam pressure, determining the steam consumption, evaporation, and the pressure of the steam from the evaporating liquid. Then a second run is made in which the steam pressure from the boiler is reduced to the value found for the steam generated by the solution in the previous run. Later a vacuum is maintained and thus through the manipulation of a single effect the data may be obtained which will give the student a more vivid idea of the design and operation of a multiple effect than the use of a multiple-effect unit itself can produce.

4. In chemical industry grinding and pulverizing is usually undertaken to hasten chemical reaction. This is a surface action and its rate is consequently proportional to the total exposed surface of the solid. The useful work done in pulverization can be measured therefore by the surface produced, and the cost of operation may be expressed per unit increase in area. It is, of course, impossible to accurately measure the total area of a mass of small particles, but a number which is proportional to it may be determined as follows: separate the material coming from the mill by either screens, settling, air separation, or other means, into a series of fractions, the mean diameter of particles in each of which is estimated (for example by measuring the screen opening). Knowing the specific gravity of the substance the weight and surface of each particle may be calculated, and knowing the weight of each fraction of the mill product, the total surface of each fraction may be obtained. The sum of the surfaces of all the fractions is the total surface exposed, and the difference between this and the total surface before the grinding measures the efficiency of the grinding operation. The application of this idea to ball mill work shows the increase in surface as a function of the time for any given conditions such as size of mill, rate of rotation, size of ball, etc., and indicates the influence which varying these conditions has upon the efficiency of the mill.

5. In the minds of most students the term "solubility table" is inextricably involved with "solubility product" or some other concept usually employed only in theoretical work. A problem in crystallization,

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fractional or otherwise, carefully planned and checked by utilization of published solubility tables clears up this misconception. The preparation of barium nitrate from Chile saltpeter and barium chloride offers an excellent opportunity to show how the solvent may be evaporated until just enough remains to hold the more soluble salt in solution after cooling. It is possible by use of data already published to separate the barium nitrate from the sodium chloride, and a problem of this sort where calculated results are checked by careful experimental work gives a thorough grasp on the principles of separation through crystallization.

6. Another problem of large importance which illustrates the phenomena of heat transfer as well as the practical applicability of the laws of heterogeneous equilibria is that of distillation. That work in a modern distillation plant, while it familiarizes one with the best industrial practice, can entirely fail to make clear the principles involved, is shown by the fact that most distillers, though good engineers, thoroughly versed in the technic of their trade, can give no qualitative explanation of the heat and concentration changes taking place in their own columns, and are unable to follow and check these changes quantitatively. The rectification of aqueous ammonia in a small plate column makes a very instructive experiment. The composition of the entering mixture, the liquid on each plate, the distillate, the slop or refuse, and the heat consumption, may be measured. The operator will determin the heat extracted by the cooling water and the composition of the partial condensate. With this data he can calculate the actual heat consumption per pound of distillate, the percentage heat efficiency of the operation, the heat transference constants of his different surfaces, the heat losses, and thus obtain the necessary information for any desired modification of the tower or still. Such an experiment shows not only how a rectifier works but why it does so, and enables him to intelligently design and control apparatus of this type.

These are but suggestions of the kind of work which we believe can be taken up in a laboratory of very modest equipment. Many others, as well as modifications of these will quickly suggest themselves to those interested in this kind of instruction. One further feature of the work which we consider very important is the preparation of a written report upon some problem, the solution of which has been attempted in the laboratory. This is not simply a recalculation or working up of data obtained during an experiment, or a more or less verbatim copy of the laboratory notes but a logical, critical, and as far as possible, convincing digest of the proposition as seen in the light of the laboratory work. The ability to write up laboratory notes in a tangible, readable, easily-get-at-able form is so uncommon with our engineering students that any exercise which stengthens his command of English is of great value.

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Every report should be so prepared both as to its English and its mechanical get-up, that it will appeal to, and be read by the busy man at once, and not be laid aside for the leisure hour which never comes.

Such a course as here outlined will never take the place of the instruction which must be obtained in a factory or works, and will not make a finished engineer; but it will contribute mightily toward giving that method of thought and work which produces the man "who knows what to do when there is something to be done."

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

POINTS OF VIEW IN THE TEACHING OF INDUSTRIAL CHEMISTRY.

BY JAMES R. WITHROW.

Received January 3, 1910.

When Prof. Talbot's kind invitation to present a paper on some phase of the Teaching of Industrial Chemistry was accepted it was done with a frank statement that the author would not have time to give this presentation the careful thought which the subject merits. The real object, therefore, of the author of these words is to get acquainted with the point of view of those who are contributing to this meeting whether on the program or helping in the discussion. He is of course glad to contribute his mite if it can assist in any way toward the desired end. After a few preliminary remarks, therefore, attention will merely be called to a few points of view in the Teaching of Industrial Chemistry which have been found of service under the conditions among which the speaker finds himself.

In a discussion of the teaching of any subject there would probably be almost as many opinions expressed as there were teachers present. If this is true of any subject it must be peculiarly possible in the case of Industrial Chemistry because of the well known magnitude of the range of the application of chemistry to the industries. It seems that what differences of opinion may exist among teachers of this subject are largely due to the fact that individual experience has differed so much, the range of possible experience being so great.

In the Teaching of Industrial Chemistry as in probably every other subject the problem which presents itself to the teacher may be summed up in the two questions:

What shall I teach?

How shall I teach it?

Ignoring the first in the brief time at hand with the assumption that what is meant in our topic by Industrial Chemistry is the study of the manufacture of chemical substances or the manufacture of commercial products with the aid of chemical processes, the present remarks will be confined merely to a few points of view with reference to the How.

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As a student your speaker had the opportunity of receiving a course of lectures on Industrial Chemistry based on the good old historic method of taking up a more or less general account of each of a series of chemical industries. After having been out in chemical manufacturing long enough to be made responsible for the running of one of the company's processes, distinct convictions were acquired as to what additional service might have been rendered by the course in Industrial Chemistry in addition to the *much* which had been so rendered.

Lecture Work.

This experience, therefore, gives the speaker, as a teacher, more to do than the mere presentation to his classes of a series of descriptions or facts concerning Industrial Chemistry which, valuable as they are, yet often appear as interesting to the student as a chapter of genealogies in the course of ordinary reading. If the industry and its vicissitudes are merely described, that is one method. If, however, each industry is taken up as an industrial problem upon which much work has been done, and still more must usually be done, then this study becomes a different matter. Then we are giving the student an attitude of mind, we are making him accustomed to habits of thought that will add much, indeed, to his industrial efficiency.

In our lecture work, therefore, let us state the industrial demand. Discuss the chemistry available and possible in connection with the case whether it be the utilization of a by-product or the supply of a commercial requirement. Then point out the reactions used and the reasons for their selection and the objections to those rejected. Then the details of the process usually employed may be discussed and as the difficulties are encountered it becomes at once apparent why so many inventions and improvements have been suggested in most cases, for it is these latter which so cloud the main issue of the industry in the mind of the student.

Then last, and probably most important of all, it is extremely helpful to the student to insist on his taking each industry and analyzing it with reference to the operations involved, as calcination, distillation, condensation, crystallization, etc. This gives him practice in just the sort of thing each keen industrial chemist intuitively does when he works out the problem of accomplishing a given industrial performance. For instance, it is expected of each student that he shall see that the manufacture of nitric acid consists, in the main, of a series of problems which may be classified under the operations of *distillation* and *condensation*. Under these two heads fall naturally the different forms of stills on the one hand and different inventions relating to condensers on the other. A little experience with this method of analyzing and broadly classifying the operations involved in a given industry not only simplifies more complicated industries but offers a simple way of linking up

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the engineering problems involved in the industry with the chemical ones.

It was the good which results from this method of study which was so sorely needed when your speaker came into his first industrial responsibility. There was utterly lacking the efficient mental classification of the whole galaxy of industries by the operations involved which this point of view would have afforded.

Laboratory Work.

With regard to the laboratory work in connection with the teaching of industrial chemistry your speaker must confess he was at first quite dubious of its value. It seems now, however, that this feeling was the result of inexperience. As a student he had not had such a course and when he began the teaching of Industrial Chemistry there was no accompanying laboratory work. It did not take long, however, after giving the subject serious consideration, to recognize the opportunity it affords of making the future industrial chemist more efficient. To be sure much labor was required, indeed much more than any one, who has never started laboratory work in this subject can even imagin. The selection of suitable problems to develop and illustrate specific ideas or points of view in the mind of the instructor and still be within the scope of feasibleness in a university laboratory is a surprisingly vexatious task.

Your speaker believes thoroughly in the principle that the student should be thrown as often as possible into association with the "tools of the trade." He should learn to know a filter press for instance like a book and if the time permits nothing further than familiarizing the student with the efficiencies of such machines, much has been accomplished. He believes just as firmly, however, that the mere knowledge of tools is not the highest end to be accomplished. This familiarity should be acquired almost as a mere incident to the solution of certain definit problems. Without taking up your time with specific illustrations, of which many probably suitable ones will present themselves from the experience of any manufacturing chemist, your speaker will merely emphasize the point of view of the *chemical part* of his industrial chemistry laboratory work at Ohio State University.

As far as the student is concerned the work is *industrial research*. As an incident in this point of view he is first made to study the cost to him of making a given laboratory preparation. After a thorough discussion of the factors which influenced this cost he has a more adequate foundation for studying industrial costs and is better able to appreciate many otherwise unintelligible variations in industrial operations. He now has obtained some familiarity with the greatest factor which will influence his decisions in all his future work.

The next step is to take up problems on the industrial utilization of

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wastes or production of materials in commercial demand. The idea is *constantly* before the student that he is *acquiring data* which will enable him to try out on an industrial scale any experiment or operation which he decides to be most promising. He soon realizes his inability to proceed at once with any experiment on a large scale with merely the information and assistance of even the most thorough fundamental chemical principles. This acquirement of a realization of the inadequateness of relying upon any mere theoretical information which he may have acquired in order to launch *at once* upon a works experiment is a big step toward starting him into some measure of industrial efficiency.

The student then very quickly gets the realization that it is *his* business to inform himself as thoroughly as posssible as to the assistance to be obtained from all theoretical and practical work which may have been done on his problem. This forces him into a diligent use of the library. When he emerges from his search of the literature he has usually found many things of importance to him. He always emerges, however, with the realization that much laboratory experimenting must be done before he can say definitly what size crystallizing tank to order, for instance, because he must determin in many cases for himself to what specific gravity the solution must be evaporated to give the most efficient crystallization. In fact he is astonished at the multitude of such points of *evident prime* importance to the success of the object in hand, which he must dig out for himself in the laboratory. He learns at once to be glad of all the assistance which solubility tables and abstract researches afford, especially after it has been pointed out to him that so-called pure research must not be expected to sound the depths which he may often require. Since its object is usually more general than his demands it often goes deepest where he least needs to penetrate. This serves to show him that he too must ever be a research man and be prepared to take up his work where pure science leaves off.

In the time allotted to such work as industrial chemistry the amount of work performed by the student is not great, but he has at least come to a realization of a number of things which cannot well help but increase his personal efficiency.

He has become acquainted with methods of attacking problems. He has acquired some familiarity, even if only to a limited extent, with the kind of thing he may expect to meet in manufacturing chemistry. He has become acquainted with the proper attitude toward his science and has obtained especially an appreciation of the potential value which may be stored up for him in all forms of scientific research, however abstract. He has come to see that the only gap between pure and applied science is the one caused by the fact that there have been too few laborers for the harvest. This respect for and appreciation of the work of others

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seems to your speaker to be often a stranger to the student of pure research if the remarks and criticisms one hears so constantly are any criterion.

Finally the student acquires from day to day the conviction that by diligent application to *all* his university work he is preparing himself for the grave responsibility which the acceptance of industrial service involves.

OHIO STATE UNIVERSITY, COLUMBUS, OHIO.

THE USE OF THE BLUE PRINT IN THE TEACHING OF INDUSTRIAL CHEMISTRY.

BY FRANCIS C. FRARY.

In the teaching of industrial chemistry and similar subjects the problem of familiarizing the student with the machinery used in the chemical industries is one which must always be met. If we had an ideal textbook for such a subject, with a large number of clear, accurate illustrations, well described and showing the parts drawn to scale, the problem would be much simplified. But that is perhaps too much to ask, since the cost of such a work would be large and the number of copies sold per year would be small. Frequent revision would be necessary, and there would be nothing in it for the author. Since we have no such book, and no prospects of it for several years, we must meet the needs of the student in some other way.

The simplest and easiest way of doing this, from the instructor's point of view, is to refer the student to some book or journal in the library which gives the desired information. But most of the students will have so much else to do that they will scarcely glance at the article, if indeed they go so far as to look it up at all. Another method, very widely used, is for the instructor to sketch upon the blackboard, from his notes, the important parts of the machine under consideration, and give the student time to copy the sketch. The original drawing which the instructor selected to illustrate the apparatus may have been very fine, but it would usually be hard to identify it as the source of the sketch in the student's note-book. Much valuable time is thus wasted in giving the student a very inadequate idea of what he should know. And in most cases, after the sketch has reposed in his note-book for a year, he could not tell what it was all about.

Perhaps the chart method may be mentioned as the next step in advance. Here, at least, we have finished originals, full of detail, often in realistic colors and of large size, and the student may copy them to better advantage. But the lecturer has nothing else to do while the student is copying the chart, so he usually takes that time to explain to the class the details of construction and operation of the apparatus. If the student takes time to copy the drawing, he misses the explanation, and *vice versa*. And even if he does his best at the copying, the result is still likely to fail

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to show many important details, and to be out of proportion and misleading. Then too the original charts are expensive, and most of those for sale by supply houses are either far behind the times, or else show foreign practice, which may be entirely different from that of the American industry. On account of the cost of the charts, too, a set once purchased will probably be used as long as it keeps up a respectable appearance, and the antiquated machinery becomes yearly more so as it is inflicted upon successive classes.

Lantern slides which may also be purchased or made to order have similar drawbacks, with the additional one that the student must copy them in a poor light, and the instructor seldom thinks it is worth while to show only one or two slides, when they are all that bear on the day's lesson.

The idea of giving each student blue prints of the apparatus under consideration, and having him paste them in his note-book, appears to have originated, as far as I can ascertain, with Dean W. R. Appleby, of the Minnesota School of Mines, who has used this method in the classes in metallurgy for some time. Knowing from personal experience in such classes how valuable the system is from the student's point of view, the author has applied it for several years to the teaching of industrial chemistry and electrochemistry, and believes it to be well worth the attention of others interested in the same line of work. From articles published in various scientific journals, from the advertisements in some of them, from patent specifications and the catalogs of manufacturers it is easy to get drawings, sections and photographs of almost everything desired. The negatives once made from these, the instructor can have the janitor or the laboratory boy make as many prints as desired for the use of the class. If advantage be taken of the summer sun, the printing process is very rapid, especially if the negatives be made upon wet-plates. The paper costs only about five cents per square yard, and the prints, neatly stored away in envelopes, are always ready for distribution.

In this way no time is lost in the attempt of the student to draw something which he has never seen, and he has an accurate picture, in proper proportions, which shows the important or peculiar parts of the apparatus. All sketches are alike, and, if desired, where the parts are lettered, the descriptive matter or list of parts may be included in the blue print so that the student may study out the construction and operation of the machine at his leisure. The student, having a good original in his note-book, can be held responsible for a fair knowledge of the machine and be required to make a sketch of it later in a quiz, and he has something in his notes to which he can refer at any time with certainty. When enough prints are to be distributed to make it worth while, a lantern slide corresponding to the blue print is a great help, as the details can be

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more readily pointed out to the student, while he still has the copy to put in his book.

Although satisfactory results may be obtained by the use of process plates, or even of any slow plate in the making of the negatives required, still where many plates are to be made at the same time, the quality of the results and the speed of manipulation place the wet-plate in a class by itself. Not only are the resulting prints more contrasty, and thus more like the black and white originals, but the negatives will print in a fraction of the time otherwise required, and far less care is needed to get a good print. In reproducing a line drawing, an over-exposure of 100 per cent. does not materially injure the print from a wet-plate negative. With rapid paper, printing takes about a minute, and three or four frames will keep a man busy.

By using blue prints it is easy to keep up with the times and add new things as they appear, without much labor or delay, and this method would seem to have advantages over all others for teaching the construction and operation of industrial machinery.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN

THE ACQUIREMENT OF PROFICIENCY IN QUALITATIVE ANALYSIS.

A DIGEST OF PRESENT AMERICAN IDEAS.

BY HERMON C. COOPER.

The scope of a thorough course in qualitative analysis seems to be such an unsettled matter that I have sought to ascertain by correspondence the current American opinions regarding it. The majority of those asked have replied, and all the replies (twenty in number) have shown great interest but no unanimity of opinion.

Notwithstanding that a large amount of thought has been given to the analytical methods of qualitative analysis rather little attention seems to have been paid to the scope and ultimate value of the course. The problem of a thorough course is one of pedagogical concern rather to universities that develop professional chemists than to the independent colleges and other schools that afford liberal education. Moreover it is a different problem in America from what it is in Germany, where qualitative analysis is the main feature of the introductory practicum.

A thorough course will be generally regarded as including practice in the reaction tests and systematic methods of separation of about twenty-five metals, the same for at least thirty acids, a brief study of selected preliminary dry tests and a presentation of a systematic procedure of "dissolving," *i. e.*, preparing materials for analysis in the wet way. The instructor easily follows the beaten path through the complete analysis of simple salt mixtures and his class is consequently introduced to the

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practice of qualitative analysis in a thorough and satisfactory manner. Such an introduction, however, is not generally considered sufficient for the prospective chemist and practice is given with various materials occurring in nature and the arts. It is obvious, I think, that, the forepart of the course being well taught,[1] the thoroughness of the course depends on the extent and character of this final practice with miscellaneous examples. Shall this final practice be extensive, including (say a dozen) truly miscellaneous natural and commercial materials, some hard to decompose and containing traces; the student's report to be essentially correct and to include all ingredients whose presence can be detected by the methods pursued; *or*, shall it be brief, confined to three or four typical minerals and commercial products, with a necessary allowance made for the inexperience of the student when the report (75 per cent. correct, for instance) is accepted. In following the second alternative the instructor may point out that experience will show that certain types of substances (*e. g.*, native silicates) rarely contain certain ingredients, wherefore the intelligent analyst will often employ a selected, limited procedure, and, further, that the subsequent quantitative procedure of analysis will shed much light on the qualitative composition.

The replies from some professors are colored by local conditions. Thus a limited allowance of time dictates the answer in a few cases. This is a serious and effective, but scarcely fundamental, argument. Most chemistry curricula are in such an evolutionary state that an early opportunity for readjustment of hours can be depended on.

The expense of supplying the necessary platinum crucibles is an argument for brief practice from the teacher in a large state university. This will be encouraging to the smaller and the richer institutions.

In general the replies favor the extended training by more than two to one. However, the difficulty of reducing the question to simple terms makes it hard for any one to give a categorical reply, and it should also be pointed out that many of those experienced in industrial analysis hold the minority view.

Professor TALBOT[2] favors a course designed to give an intelligent knowledge of the usual systematic procedure with a limited amount of practice with the more complex and less soluble materials. "It is obvious," he says, "that qualitative analysis is a portion of our science in which a man may profit by long and varied experience, and I think that every student should have had some experience in the analysis of a complex

[1] Implying careful attention to the laws, properties and reactions involved, to the solubility differences as the basis of separation and to manipulation, as well as to logical reasoning.

[2] All opinions quoted are regarded as personal, not institutional and not necessarily representing the present teaching practice in the institution to which the person belongs.

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and, perhaps, refractory mineral and be held for a considerable degree of accuracy; but, if he has been trained to work intelligently and neatly, it seems to me probable that he will adapt himself quickly to any one particular line of material with which he later comes in contact as a part of routine work." The varied nature of qualitative problems makes it seem to him more a question of chemical intelligence and ingenuity than of reproducing the experiences of the instructional laboratory even in the case of the practicing analyst. He would "rather require a real familiarity with the chemistry of the analytical scheme, such as would make the analyst watchful and critical, than to increase the number of unknowns to the extent suggested."

A manufacturing chemist of extensive analytical experience (Mr. J. T. BAKER) considers fewer miscellaneous exercises preferable because we then "give the practicant a general idea of qualitative analysis while at the same time enabling him to cover more ground and thereby broaden his mind instead of wasting much useful time in his effort to work out vexing and unnecessary problems * * * quite different from those he will encounter in practical work outside." "The object sought by the practicant is not a mechanical training but an education," one that will make him "familiar with various lines of scientific work and necessarily so, for the problems that confront the chemist are not wholly chemical, but are physical, mechanical, electrical and even temperamental."

Dr. L. C. JONES writes in a similar strain, considering the essential things to be "familiarity with chemical methods, habit of accuracy and absolute confidence in results obtained." He thinks that the essential facts might be taught by typical salt solutions, and work upon commercial materials possibly delayed until the student reaches quantitative analysis.

Professor DENNIS also favors fewer miscellaneous exercises. Dr. J. E. TEEPLE thinks that practice in the analysis of mineral or commercial products should be a mere incident as compared with a fundamental knowledge of the reactions.

It appears to be the idea of these men that experience with concrete unknowns is decidedly secondary to a study of the chemistry and application of the systematic scheme. Indeed qualitative analysis seems to be regarded by some as an essential part of the laboratory course in general chemistry. The writer (COOPER) thinks that American opinion is trending in the opposit direction.

Turning next to the contrary opinions: A teacher in a large university says we should aim to equip the student to perform an exhaustive qualitative analysis; "otherwise how can the course be called 'thorough' " and he quotes Prof. A. A. NOYES[1] to the effect that inability to make a

[1] Noyes and Bray, THIS JOURNAL, 29, 141 (1907).

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good qualitative analysis is a common source of error in quantitative results. To accomplish this the said teacher advises giving the student a number of minerals, commercial products, etc., involving some rather small percentages.

In a similar strain Prof. W. T. HALL adds: "The final verification in the quantitative analysis by its summation to 100 is unsatisfactory. Often a substance like tin-stone is called 'silica,' etc. . . I agree with Professor HILLEBRAND[1] that 'frequently the analysis is entrusted to a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals and with a laboratory instructor as adviser, whose experience in rock analysis may be little superior to his own. In other words: one of the most difficult tasks in practical analysis is expected to be solved by a tyro.'" Professor HALL points out also that "a great deal of chemical inspiration can be imparted to a student and training for scientific investigation given by a thorough course in qualitative analysis where the work is made as varied as possible."

The replies of Profs. A. H. GILL, G. B. FRANKFORTER and L. W. ANDREWS are similar to this. Some technical chemists also support this view. Mr. W. D. RICHARDSON reminds us that "a student learns his general chemistry only after he has studied qualitative and quantitative analysis and thus the longer and harder course would have an indirect bearing of the greatest importance. Dr. Teeple, however, discredits the latter clause.

One of our best known consulting and analytical chemists Dr. S. P. SADTLER, writes: "If it is the design to equip the young men to make successful applications for the wider range of positions that offer in the manufacturing and commercial world, they should have an opportunity to see and exercise their power upon a moderate list of technical products. These need not be very complex mixtures, but they ought to be such substances as he would have put into his hands for analysis when he takes the position of chemist for a manufacturer or dealer in materials that have to be tested." This position seems to occupy middle ground in the discussion. Incidentally Dr. SADTLER strongly urges instruction in what is called a proximate analysis, as distinguished from an ultimate one, and the inclusion of organic analysis, saying that the student should learn "the selective action of solvents and how to apply class reactions as means of identification of the constituents of a mixture."

Prof. J. H. WALTON, JR., in charge of qualitative analysis at the University of Wisconsin, points out the desirability of requiring detection of small quantities from a standpoint of manipulation. "Moreover," he writes, "so much of practical qualitative analysis deals with the detec-

[1] U. S. Geol. Survey, *Bull.* 422, 16 and foll.

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tion of mere traces of impurities." It seems to him that "after the student has had a certain amount of his qualitative work, he should be able to eliminate certain constituents for himself. For example, if given a silicate, he ought to see that such a thing as potassium iodide would not be present."

Prof. L. W. ANDREWS observes *apropos* "that the student will be sufficiently prone to omit everything that can be omitted, without receiving special stimulation in that direction."

Nevertheless, there is considerable practical value in being able "to eliminate certain constituents." One of our best analysts among manufacturing chemists (Mr. G. P. ADAMSON)—apparently favoring fewer miscellaneous analyses—thinks that the student should be taught to analyze the given materials "in accordance with the composition of the ores or rocks as found in nature, testing only for the ordinary constituents, *e. g.*, in copper ore, testing for copper, silica, iron, arsenic, silver and gold. The finer points in the analysis and rarer elements will be determined afterward when a quantitative analysis is made." He would not necessarily use the summation to 100 as a test. Indeed he would probably agree with Dr. TEEPLE that "a complete quantitative analysis is the exception rather than the rule."

We do well, therefore, to stop at this point to consider what is meant by these modified analyses, or *intelligent analyses*, as we may call them. Dr. F. W. CLARKE deals with the problem vigorously in his introduction to "Analyses of Rocks and Minerals."[1] He deplores the old form of "complete analysis" which used to be practiced in the Geological Survey laboratory and is still followed by many. In such an analysis the constituents of direct petrographic significance were determined. The minor ingredients were incorporated with the principal ones and a summation to 100 per cent. was obtainable. Such work, according to CLARKE, is often grossly misleading and is inadequate to modern requirements, only the most refined methods of work and statement being admissible. A typical result of the more careful analyses is the discovery that barium and strontium are found to be almost universally diffused in igneous rocks.

However, it is evidently not the practice of the Survey to demand[1] that an amount of time "altogether disproportionate to the immediate objects to be sought" should be expended on every analysis. The general rule of the Survey is "that the constituents which are likely to be present in sufficient amount to admit of determination in the weight of a sample usually taken for analysis * * * should be sought for, qualitatively, at least, in the ordinary course of quantitative work and their presence or absence noted among the results. A special note should be made of neglect to look for substances which it is known are

[1] U. S. Geol. Survey, *Bull.* 419, 3.

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likely to be present." A thorough microscopic examination of the rock in thin section is often of greatest aid to the analyst. Professor HILLEBRAND writes anent this discussion, that he would not leave the student wholly in the dark with his miscellaneous unknown and so "let him waste much time in a vain search for what is not likely to be there."

It appears that it has required very extensive experience to determin what elements should be tested for in an intelligent rock analysis and one is impressed with the fact that the accuracy of all such "intelligent" analyses from a qualitative standpoint is merely a matter of probability and that we need to study the precision of our analyses qualitatively as well as quantitatively.

In the fields of the various commercial products it may be that some analysts have acquired a corresponding rich experience so that an intelligent analysis is satisfactory, but laboratory teachers are scarce who know the results of such experience in the various fields. Apparently here is an opening for a new manual as a guide to intelligent, or classified, practical analysis. Without a guide the practice work of the student would require a wholly impracticable amount of time.

The *general verdict* of this symposium is difficult to ascertain because of the modifications and digressions introduced by participants, but the writer believes that the majority of teachers and experienced analysts will join in advising (1) a systematic qualitative procedure of known sensitiveness for the common metals and acids; (2) the carrying out of this procedure in all cases, unless a limited analysis is specified; (3) tests for rarer constituents (arbitrarily selected for the present; perhaps we may some day have a rapid systematic procedure for all the metals and even acids); (4) a tabulation of results that will indicate exactly what has been tested for. It may not be amiss to add that the composition of all practice unknowns must be known to the teacher and further that there ought to be a good market for such standardized qualitative unknowns of a concrete character.

However much the majority of us may desire to give a generous assortment of unknowns toward the end of the course it is very doubtful if the freshman or sophomore will profit proportionally by it. He needs mental growth more than comprehensive analytical practice. According to Professor H. L. WELLS, of Yale University, "it is hardly possible to equip the student for exhaustive qualitative analysis in his first course in the subject. He needs experience in quantitative analysis." Professor Wells would accordingly "devote much attention in this first course to formal rather than to practical, qualitative analysis;" he would, however, include some minerals, etc., as practical examples.

Later in the curriculum, perhaps in connection with his advanced

[1] Hillebrand, U. S. Geol. Survey, *Bull.* 422, 21.

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quantitative analysis, the student can be greatly enriched by a course giving the practice prescribed by the majority of our contributors, in the full and reliable qualitative analysis of varied materials. This sort of plan is followed at the University of Chicago. Two quarters are given in elementary qualitative analysis, including an exhaustive analysis of ordinary salt mixtures and twenty or more simple unknowns. "After these two quarters," writes Professor STIEGLITZ, "students are admitted to quantitative analysis and, if they intend to go into technical positions, they take later a third quarter in qualitative analysis, in which they get commercial products, ores, minerals, pigments, some rare element work, cyanides, etc." In the introductory course "special stress is laid also on instruction from the general chemistry point of view." A similar plan is probably in force elsewhere.

Those teachers who wish may also point out in the later course how the nature of the material excludes certain constituents. All should make clear the light that is afforded by the solubility observations. Furthermore, some additional theoretical applications can be elucidated and, in general, an eminently satisfactory and profitable treatment of qualitative analysis concluded. This subsequent finishing-course seems to offer a solution of the main problem of our discussion.

SYRACUSE UNIVERSITY.

SUGGESTIONS AS TO CERTAIN DESIRABLE CHANGES IN CHEMICAL NOMENCLATURE.

BY EDWARD BOOTH.

The nomenclature of chemistry is better and in every way more serviceable than that of any of the other sciences, but it is still far from perfect. It has not yet reached the point at which betterment is impossible. This paper is a plea for further improvement. In 1787, a century and a quarter ago, Lavoisier, presenting a paper to the French Academy said: "It is time to free chemistry from obstacles of all kinds which retard its progress, to introduce into it a true spirit of analysis: and it is by the perfecting of the language that this reform is to be effected." And he then proceeded in the same paper to suggest a nomenclature which was promptly adopted by the Academy, which with the few changes and additions required by the growth of the science is still in universal use and which has completely fulfilled the expectations of the great man who devised it.

It is unnecessary to enter into historical details, yet a brief résumé may not be inappropriate. Up to the time of Lavoisier's paper chemical nomenclature was in a chaotic condition very much as are those of some of the other sciences at the present time. Names had been given in most arbitrary and unreasonable ways: sometimes suggested by a physical property, or a fancied resemblance to some material in common use;

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sometimes to honor the discoverer or to commemorate the place of discovery; and not infrequently the names were given by the alchemists with the intention of conveying as little information as possible and of adding mystery to a subject which, in the public mind, was closely associated with necromancy and witchcraft. But in the latter part of the eighteenth century chemistry was beginning to emerge from its medieval darkness and the need of a better language had begun to be felt. Various abortive attempts at improvement had been made but it was not until Guyton de Morveau read a paper before the French Academy in 1782 that the subject received the attention that it deserved. Morveau's suggestions did not prove acceptable but they contained the germ of the modern system. The Academy recognized the importance of the matter by appointing a committee consisting of Lavoisier, who was then in his prime, of Fourcroy and Berthellot. These three, aided by Morveau, originated the present system, which was reported to the Academy by Lavoisier and is believed to be mainly his work.

Since Lavoisier's day few, if any, radical changes have been made. Lavoisier realized the true significance of a scientific nomenclature—that it should be founded on underlying principles and should be elastic enough to accommodate itself to the natural and inevitable growth of the science. Yet Lavoisier, sanguin as he was, could never have foreseen the wonderful growth of his loved science, nor have imagined the perfection of the name-system that he recommended. A few changes have been made in the past century but these changes, as to principle, are insignificant; and we are to-day using practically the names advocated by him. Various attempts to improve this system have been made or suggested from time to time, such as the cumbrous method proposed by Gmelin, but nothing has been found equal to the names proposed by the French committee. This paper does not suggest changes in this nomenclature, it recommends a closer adherence to it than has yet been given. We have not yet advanced quite to the point where Lavoisier stood more than a century ago. We recognize the value of a perfect nomenclature, yet we are unwilling to adopt it in its entirety. We still cling pertinaciously and unreasonably to our old errors. We still use names that should have been forgotten long ago. A century ago it was recommended that such unscientific names as oil of vitriol, butter of antimony, liver of sulfur and sugar of saturn should be abandoned and their more scientific equivalents used; but we still talk of aqua regia, cream of tartar, caustic potash, microcosmic salt and a score of others of similar character. We have nearly abandoned liver of sulfur but adhere firmly to flowers of sulfur. We do not now describe lead acetate as sugar of saturn but we haven't entirely abandoned the name sugar of lead.

My work at the University of California brings me in contact every year

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with large numbers of students who have studied chemistry in the high schools of the country. These students, when they enter the university, are supposed to have a knowledge of the elements of the subject; and it must be confessed that their knowledge is often very elementary in character. But what smatterings of knowledge they do possess are often partly neutralized by the inconsistencies in nomenclature which they have encountered. The same substances are differently named in different text books, and on entering the university are found to have still other names. One who has not had this experience cannot appreciate its seriousness to the beginner, nor can he realize the time wasted by the student in trying to ascertain whether copper sulfate and cupric sulfate are identical and are both the same as sulfate of copper; whether there is any difference between barium chloride and baric chloride; whether he can use argentic nitrate when his instructions are to use nitrate of silver or silver nitrate. Every one who has had dealings with beginners has had like experiences. And the fault is by no means confined to the elementary schools. It is wide-spread and is, in many cases, the result of carelessness. Old labels and old names are apt to remain even on university shelves; and a student is to be pardoned if he thinks that potassium has a higher valence behind a label of "potassic hydroxide" than behind one of "potassium hydroxide," or if he becomes completely befuddled in trying to ascertain how arsenic trioxide contains less oxygen than plain arsenic oxide. I recently glanced over a number of text books prepared for high school use and noted the variety of names used and the entire lack of harmony. Such variations as caustic soda, sodium hydrate and sodium hydroxide were practically universal and in one case, that of hydrogen sodium carbonate, I found six different names used. Of course, at the same time, it must be stated that in most cases the proper scientific names were used.

I realize that to an older chemist, one who has passed far beyond the alphabet of the science, these criticisms may seem trivial; but to the beginner such difficulties are very real and discouraging; and, as Lavoisier said a century ago—"it is time to free chemistry from obstacles of all kinds that retard its progress."

There is really no good reason why these inconsistencies should continue to exist. We know better and have known better for more than a century. We fully realize the superiority of the scientific method but we do not put it into effect as completely as we should. We use names that should have been long consigned to the rubbish pile, and we do not even use the scientific names themselves with the proper care.

There can be no question as to the desirability of reforms in these directions—the only question being as to the best way of bringing them about. Possibly the most efficient way would be the adoption by the American

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Chemical Society of a standard nomenclature. A committee appointed for this purpose could make a report which, if adopted by the Society, would be gladly adopted by the majority of chemists in America. I have suggested a few of the inconsistencies that exist. Some of these might not prove of sufficient importance to correct, and, undoubtedly many exist that I have not pointed out.

In 1881 Prof. A. W. Williamson presented to the British Association for the Advancement of Science a paper somewhat similar in purpose to the one now presented for your consideration. As a result, a committee on the reform of chemical nomenclature was appointed, containing, among others, such eminent men as Roscoe, Dewar and Frankland. Reports were presented on three successive years, 1883, 1884 and 1885. The first of these was merely an application for more time. The others contain much interesting matter and a number of tabulated statements showing the variety existing in the use of different names, but unfortunately not making explicit recommendations for reform. The reports are really more useful as showing the need of reform than as suggesting remedies. Two years before Williamson presented his paper, Watts, who was editor of the Journal of the London Chemical Society, issued a set of instructions on this subject to be used by abstractors of that Journal and if these instructions could be adopted by the American Chemical Society even without change, they would greatly improve the conditions at present existing. It is interesting, as illustrating the lack of harmony existing, that whereas Watts instructed abstractors to use the term "normal" in connection with salts formed by the complete replacement of the hydrogen of an acid, instead of the term "neutral;" yet exactly the opposit use occurs in the report of the eminent chemists who made up the committee of the British Association.

If such a committee as I have suggested should be appointed, its recommendations would, of course, meet with opposition, but opposition never yet prevented the ultimate adoption of improvements. Some chemists of the present day are, undoubtedly, as conservative as their progenitors of a hundred years ago, and will urge the retention of old names like aqua regia merely because they are old. Lavoisier's report had hardly been published before opposition arose. In the *Annales de chimie* for 1789 is a long account of the criticisms made by Gadolin, who asserted that as every one knew the old names, only those should be abandoned that are obviously absurd. And as an illustration he states that every one knows that the saline substance formed by the action of vitriolic acid with a metal is called a vitriol; and he thinks it unwise to change such well-established names, recommending the retention of these names in a slightly modified form as vitriolum potassae, and he further suggested the formation of new names by the use of such terminations as

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"atum," "as" and "is;" and he gives as illustrations "phosphoratum ferri," and vitriolas ferri "and vitriolis ferri." Opposition of this kind is to be expected at all times, but may be disregarded.

It is useless to try to present a full list of the existing inconsistencies. The number is larger than one who has not considered the matter would think. But if such a committee as I have mentioned were appointed, I should recommend that it take action on such points as these:

1. That old, unscientific names, many of which are of alchemical origin, should be replaced by their scientific equivalent. This would include such names as aqua regia, microcosmic salt, borax, red lead, magnetic oxide of iron, cream of tartar, tartar emetic, caustic soda, and a score of others.

2. That a definit usage of scientific names be recommended to overcome such inconsistencies as I have already referred to. In his "instructions" Watts recommends that all chemical names be written without the terminations "ic" or "ous," unless it is intended to indicate the valence, and that names like "potassium hydroxide" be used instead of "potassic hydroxide." Such a definit system would be a welcome change.

3. That proper prefixes and suffixes should be used, or where more than one can be used, a selection should be made. Originally "bi" was applied wholly to the negative part while "di" played a corresponding part with the positive. So that "potassium bichromate" was something quite different from "potassium dichromate." It may not be advisable to return to the older usage, but at any rate it would clarify the language if one of the two terminations were abandoned. And this is merely an illustration of numerous similar cases.

4. The partly scientific names given to many substances should be revised so as to make them conform to good usage. This would include such names as silica, alumina, hydrogen sulfide, and probably arsine, phosphine, stibine, etc. In fact the names of the hydrogen compounds are badly in need of scientific revision. Possibly, too, at this place would come such meaningless names as alcohol and acetic acid. Of course, right here, opposition would be very strong.

5. The names of many of the laws and theories should be revised so as to make them as scientific as the names of materials. There is no more reason why a certain doctrin should be called Avogadro's hypothesis than that a certain salt should be called Glauber's salt. We have recognized the folly of the system in connection with the salt; it is time to recognize the folly in connection with the theory. Avogadro and the other discoverers are entitled to all honor, but let us honor them in some other way. Do not let us interpose obstacles in the study of chemistry as a method of honoring these men.

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6. The question of reformed spelling should be considered. When a student learns that a sulphide is a very different thing from a sulphite and a sulphate he surely should be pardoned if he thinks that a sulfide is a representative of still another class and a sulfid of a fifth.

I offer these suggestions in the hope that, even if not acted on at the present time, they will cause thought and may be acted upon in the future. I am firmly convinced of the desirability of most, if not all of the changes suggested and I am also firmly convinced that such reforms would make the study of the science far easier for beginners; would remove some of the obstacles to which Lavoisier objected so strongly; and would make the nomenclature of chemistry more nearly perfect than it now is.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CAL.

Some of the points which are covered in the preceding paper have already been provided for in the usage of the Journal of the American Chemical Society and Chemical Abstracts. Especially, these journals never use the ending "ic" for elements which have only one valence or where the valence is not specifically in mind. Thus the words potassic and argentic are never used. Also the term hydrate is never used where hydroxide is intended. A good many rules which are followed in these journals will be found in the Directions for Abstractors, which were published in Chemical Abstracts for June 20, 1910. These rules, in the main, follow the usage of the London Chemical Society and are designed to secure as complete uniformity as possible in such matters. Some of the other points brought up by Professor Booth will be considered later by the Board of Editors of the Journal of the American Chemical Society, to whom the question was referred at the Minneapolis meeting.—EDITOR.

INSTRUCTION IN PHYSICAL CHEMISTRY: TWO MODIFICATIONS.[1]

BY RESTON STEVENSON.

In teaching physical chemistry at the College of the City of New York, there have been advantageously introduced two practices which are not common. The first is the use of a station for each experiment instead of a desk for each student; the second is the study and tabulation of the errors involved in each experiment.

1. *The System of Stations.*—No student has a desk with a meager assortment of apparatus that is seldom used. Instead, there is arranged in a series of desks, a large and varied collection of all kinds and sizes of chemical apparatus. In this way, any student has at his disposal a sufficient amount and large diversity from which to make his selection and

[1] Communicated with the sanction of Dr. Charles Baskerville, Director of the Dept. of Chemistry, College of the City of N. Y.

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he learns about chemical apparatus and how to select forms for his particular needs.

The experiments are arranged very much as in physical laboratories and not as in chemical laboratories. There is a station at which each experiment is to be performed, where the apparatus is collected and sometimes assembled (as in the case of thermostats). Supplementary to each station is a desk which contains for that experiment the appurtenances such as chemicals, finer apparatus, special directions, references, notes, curves, etc. In this way the laboratory accommodates an indefinit number of students who move about from station to station. The student is required to assemble and construct only enough apparatus to teach him laboratory technic. There are also stations for glass manipulation, blast lamps, hot plates, steam baths, mercury purifiers, reagents, chemicals, gas generators, etc., in commission.

2. *The Study of Errors.*—Manuals of physical chemistry are satisfied in their consideration of errors when they explain the meaning of the "probable error." This is important but not adequate. Every experiment performed in a scientific laboratory is a measurement and in making a measurement, it is of first importance to know in what ways and to what extent the measurement is misleading and how this divergence can be avoided or remedied. To understand an experiment, therefore, we must know the sources of errors, their magnitude and their correction. From such a tabulation of errors, one can decide how to proceed for the rapid approximate measurements and how for slower, precise determinations. At the end of every report of an experiment the student submits a tabulation of errors, divided for convenience into (*a*) errors of manipulation and (*b*) errors of apparatus and method. The arrangement of such a tabulation is indicated below.

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(*b*) ERRORS OF METHOD AND APPARATUS.

Source.	Magnitude.	Correction.
Variation of the concentration of the solution. The freezing out of ice.	< 3%, +	Calculate from the amount of supercooling, the weight of solvent frozen out and subtract from the weight of solvent taken.

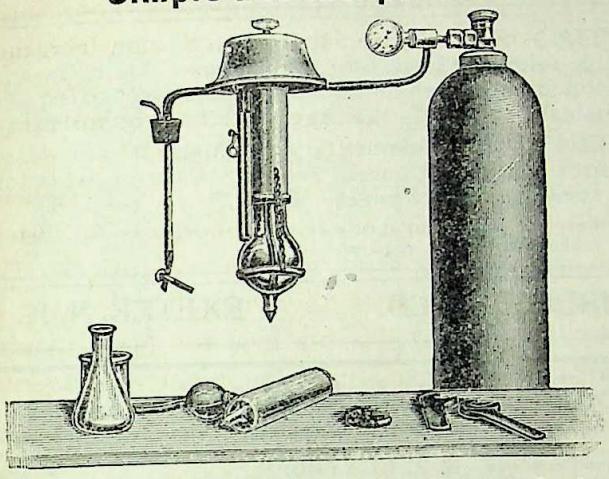
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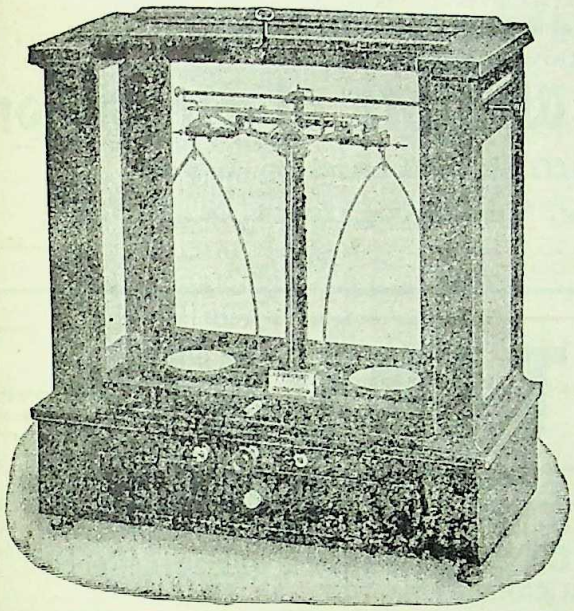
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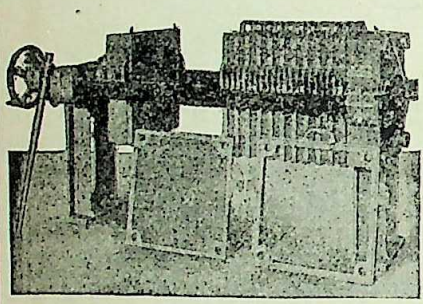
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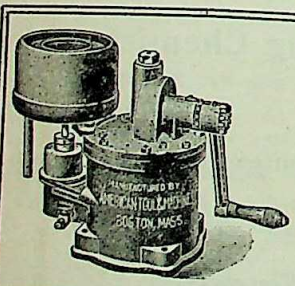
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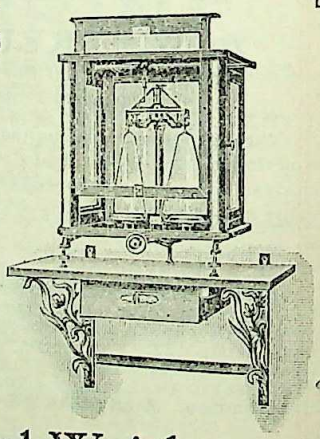
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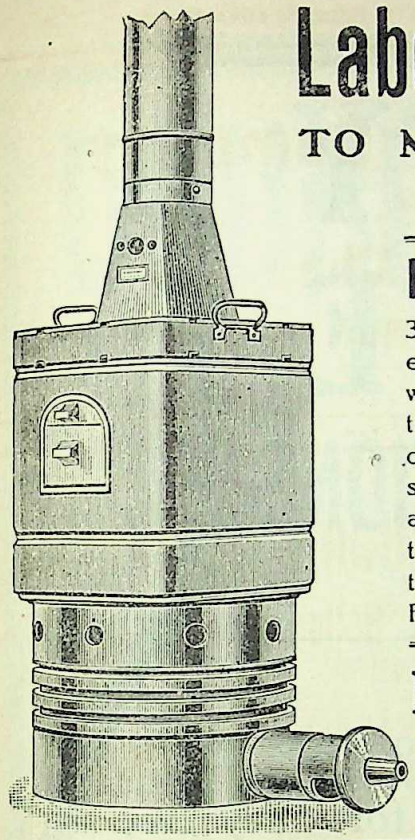
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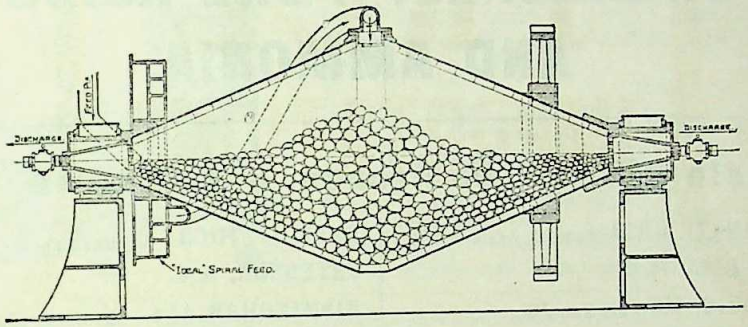
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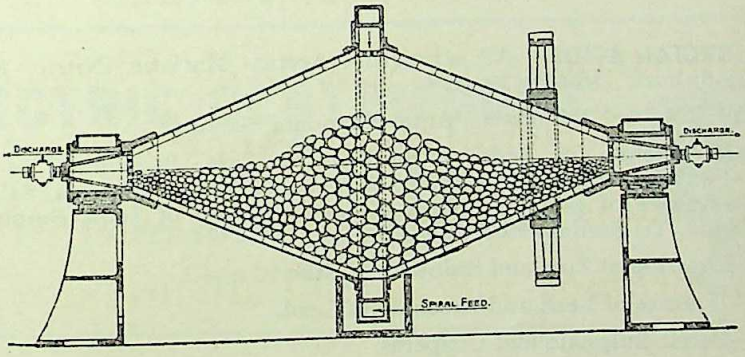
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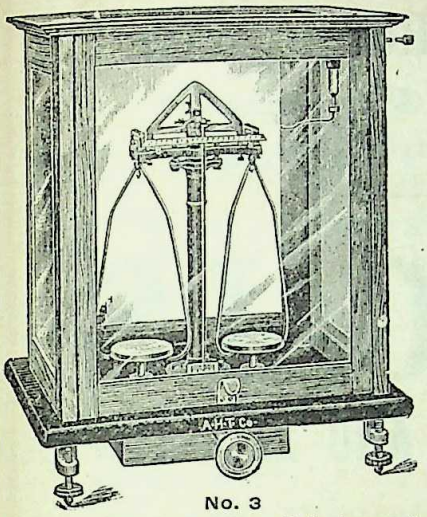
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Is the Largest Society in the World covering any one science and that ITS THREE JOURNALS reach more Chemists and Chemical Industries than any other publication.

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Issued with the May Number, 1911.

Proceedings.

COUNCIL.

By letter ballot counted on April 4, 1911, the Council authorized the formation of the Connecticut Valley Section of the American Chemical Society with headquarters in the city of Hartford and territory included within a radius of thirty miles of that city.

At the same time the Council elected the following associate editors of the *Journal of Industrial and Engineering Chemistry* as recommended by the Editor-in-Chief.

BARNARD, H. E.,
BRADY, WILLIAM,
BAILEY, E. G.,
BARTON, G. E.,
CARPENTER, F. B.,
COBLENTZ, VIRGIL,
GEER, W. C.,
HILLEBRAND, W. F.,
HORNE, W. D.,
LANGENBECK, KARL,
LITTLE, A. D.,
LUCKE, C. E.,
MATTHEWS, J. MERRITT,
MCCREADY, ERNEST B.,
MCILHINEY, P. C.,
PARKER, T. J.,
RICHARDSON, W. D.,
STONE, GEO. C.,
WAHL, ROBERT,
WALKER, W. H.,
WHITNEY, WILLIS R.

CHARLES L. PARSONS, *Secretary*.

MEMBERS ELECTED BETWEEN MARCH 15TH AND APRIL 15TH.

Adler, Jacob, 302 W. 13th St., New York City.
Allison, Harold B. C., 2279 Massachusetts Ave., Cambridge, Mass.
Armitage, Lacey H., 40 Johnson Ave., Newark, N. J.
Ashley, R. Harman, Deer Lodge, Mont.
Baker, E. L., 369 Castle St., Geneva, N. Y.
Baker, Henry F., care Thomsen Chem. Co., Baltimore, Md.
Barden, Alfred, Shelley, near Huddersfield, England.
Barol, Alfred, 613 Pine St., Philadelphia, Pa.
Battista, A. A., Tenino, Wash.
Bellamy, Harry T., 2712 Jackson St., Omaha, Nebr.
Bonney, V. B., Pullman, Wash.
Campbell, William B., 4355 Montrose Ave., Westmount, Que., Canada.
Carter, Louis H., Delta Upsilon House, Tufts College, Mass.
Casler, H. L., 137 John St., Utica, N. Y.
Chance, Clinton F., care Chance & Hunt, Ltd., Oldbury, England.
Cheetham, Charles Lee, 88 Webster St., Lewiston, Maine.
Conroy, Henry J., 182 Blue Hill Ave., Roxbury, Mass.
Cothran, John C., 2 Pine St., Arlington, N. J.
Croswell, Volney R., 916 E. Washington St., Ann Arbor, Mich.
Cummings, Herbert K., Alfred University, Alfred, N. Y.
Davis, Richard F., 221 Eddy St., Ithaca, N. Y.

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Derr, H. A., Lexington, Virginia.
Engelhardt, H., 2910 Garrison Ave., Forest Park, Baltimore, Md.
Finn, Alfred N., Bureau of Standards, Washington, D. C.
Fisher, Joel Ellis, Jr., 460 Yale Station, New Haven, Conn.
Fisk Rubber Co., Chicopee Falls, Mass.
Frank, Joseph Otto, Winona Lake, Ind.
Frazer, John, 928 Spence St., Philadelphia, Pa.
Glaser, Henry, 750 Castro St., San Francisco, Calif.
Glasoe, P. M., St. Olaf College, Northfield, Minn.
Hambly, Fred J., Buckingham, Que., Canada.
Hawkins, Lon A., Bureau of Plant Industry, Washington, D. C.
Hendry, Johnson F., 66 Thirteenth St., Troy, N. Y.
Heppner, Otto B., 317 North 9th St., Terre Haute, Ind.
Holaday, Horace A., Univ. of Idaho, Moscow, Idaho.
Holsten, Frank E., 94 West 30th St., Bayonne, N. J.
Hood, Robert C., Lexington, Virginia.
Johlin, Jacob M., Jr., 5704 Monroe Ave., Chicago, Ill.
Kennedy, Frank M., 208–5th Ave., New York City.
Kerr, W. C., Catonsville, Maryland.
Lambert, Charles A., 40th and Butler Sts., Pittsburg, Pa.
Lando, M. N., 806–10th St., N. W., Washington, D. C.
Lang, Peter A., 2246 W. 98th St., Cleveland, Ohio.
Levy, Archibald L., 3238 Vernon Ave., Chicago, Ill.
Lunn, Charles A., 215 S. State St., Ann Arbor, Mich.
Mantell, Frank A., City Hall, Memphis, Tenn.
McKinnell, J. Franklin, Dept. of Health, 6 E. Franklin St., Baltimore, Md.
McNamee, Lawrence R., 533 E. University Ave., Ann Arbor, Mich.
Moody, Graham B., 2646 Dwight Way, Berkeley, Calif.
Morris, Samuel, Pullman, Wash.
Nelson, John W., Washington State College, Pullman, Wash.
Nemzek, Leo P., 322 Race St., Philadelphia, Pa.
Parker, E. G., care Royal Crown Soaps, Ltd., Winnipeg, Canada.
Paschall, Benjamin S., 664 Empire Bldg., Seattle, Wash.
Pearse, Langdon, 39th St., Sewage Pumping Station, Chicago, Ill.
Pearson, Frederick J., 3741 W. 63rd Place, Chicago, Ill.
Pope, Chester H., 39 Waldemar Ave., Winthrop, Mass.
Pratt, James B., care Southern Cotton Oil Co., Charlotte, N. C.
Randall, Wyatt W., Dept. of Health, 6 E. Franklin St., Baltimore, Md.
Reich, Gustav, 542 Main St., Niagara Falls, N. Y.
Ridenour, W. E., 2nd and Bristol Sts., Philadelphia, Pa.
Rodgers, James R., 353 Kerlin St., Chester, Pa.
Rogers, John, care Nobels Explosives Co., Ltd., 195 W. George St., Glasgow, Scotland.
Scheffler, C. C., 2274 E. 101st St., Cleveland, Ohio.
Schwarz, Edward G., 75 Schenck Ave., Brooklyn, N. Y.
Seavey, Charles M., 11 Hawes Ave., Dorchester, Mass.
Steele, Lawrence L., 17 Dean St., Worcester, Mass.
Strong, Ralph K., 5802 Jackson Ave., Chicago, Ill.
Threlfall, Richard, Oakhurst Church Road, Edgbaston, Birmingham, England.
Warren, Howard B., 839 Stuyvesant Ave., Trenton, N. J.

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Warrington, George H., Citizens Bank Bldg., Cincinnati, Ohio.
Williams, E. R., 43 Kendal Ave., Toronto, Canada.
Ziegel, Henry H., 86 Longwood Ave., Brookline, Mass.
Zinsser, Rudolph, 1 West 70th St., New York City.

BOARD OF DIRECTORS.

The Directors of the American Chemical Society met Friday night, March 17th, at 10 o'clock, at the Chemists' Club, 52 East 41st St., New York City, with President Smith in the chair and all the Directors present.

It was voted on recommendation of M. C. Whitaker, editor, and Harvey F. Mack, advertizing agent, that the price for advertizing on the front cover of the *Journal of Industrial and Engineering Chemistry* be placed at one hundred dollars per issue.

A. M. Patterson, editor of *Chemical Abstracts*, was present by request and stated to the Directors that his health would not permit him to give the same time in future to *Chemical Abstracts* as he had given in the past and that the work involved in the publication of the journal had so increased that a reorganization of the staff was necessary. After extended discussion Dr. Patterson consented to retain responsibility and continue in a supervisory capacity and it was voted that the recommendation in Dr. Patterson's letter of March 10, 1911, be adopted on the basis that he be paid a salary of $500, that the first associate editor be employed by him at a salary of $1500 and a second associate editor at a salary not to exceed $1000, all to date from September 1, 1911, and that the salary of the first associate editor be increased $16.66 per month from April, 1911, to August, 1911, inclusive.

It was voted that the Directors instruct the editor of *Chemical Abstracts* to communicate with the heads of departments of that periodical calling their attention to the rapid increase in its size, cost incident thereto and the necessity of keeping down the number and length of abstracts as far as is possible without injury to the quality of the publication.

Extended correspondence with the Post Office Department was presented to the Directors and it was voted to approve the methods of procedure determined upon by conference of the Secretary with the Third Assistant Postmaster-General and that the following changes in by-laws be recommended to the Council.

Change by-law 14 to read:

Membership in the Society is continued by the annual receipt of a combined clubbing rate subscription to the amount of ten dollars ($10.00) to the Society's publications. There are no other membership dues. Any member not wishing the journals may continue his membership by supporting the work of the General Society to a like annual amount through contribution to its treasury.

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Change by-law 17 to read:

Any person in arrears for two years shall cease to be a member until all his arrears are paid or until reinstated as a member by a majority vote of the members of the Council.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary.*

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

GEORGIA SECTION.

The Section held a meeting at the Café Durand, Atlanta, Thursday evening, February 9th, preceded by a dinner in honor of Charles L. Parsons, Secretary, who afterwards spoke to the Section on "The Value of Research Laboratories to the American Chemical Industries."

The following officers were elected for 1911: *President*, W. P. Heath; *Vice-President*, F. B. Porter; *Secretary*, J. S. Brogdon, $65^1/_2$ North Broad St., Atlanta; *Councilor*, H. B. Arbuckle.

J. S. BROGDON, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club on Thursday evening, February 23rd, preceded by the usual dinner.

The speaker for the evening was Mr. C. A. Catlin, of Providence, who addressed the meeting on "Chemical Leavening Agents."

The next meeting was held at the University Club on Thursday evening, March 30th. Mr. W. M. Saunders, of Providence, gave an address on "Iron Ore."

ALBERT W. CLAFLIN, *Secretary.*

SECTION OF WESTERN NEW YORK.

A special meeting was held at Niagara Falls, N. Y., March 10th, with President Watkins in the chair, to discuss the questions of local Sections and their relation to the general Society. After careful consideration the judgment of the Sections was formulated and sent to the secretary of the Society.

A meeting was held in the Auditorium of the Natural Food Co., Niagara Falls, N. Y., on April 4th, at 8.15 P.M.

Mr. J. Horace McFarland gave an address and held debate with members of the Section upon the "Conservation of Niagara Falls."

WALTER WALLACE, *Secretary.*

INDIANA SECTION.

The Section met in the office of the Indiana State Food and Drug Laboratory, Friday afternoon, March 10th.

Papers were read on "The Composition of Creosote Oil," by P. N.

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Evans, of Lafayette, and "The Manufacture, Use and Testing of Vitrified Paving Brick," by W. M. Blair, of Indianapolis. A. D. THORBURN, *Secretary.*

ST. LOUIS SECTION.

The regular March meeting was held on Monday night, the 13th, at the St. Louis Academy of Science Building. Mr. J. J. Kessler gave an account of "The Preparation of the Nitrile of Fumaric Acid." Then Professor W. H. Warren spoke on "The Examination of the So-called Sugar Sand Obtained from Evaporated Sap of the Sugar Maple Tree." Dr. Warren showed that this "Sugar Sand" or "Niter" consisted largely of neutral calcium malate. On February 18th a dinner was held, which was largely attended by the chemists of St. Louis. R. NORRIS SHREVE, *Secretary.*

PHILADELPHIA SECTION.

The regular monthly meeting was held at the Engineers' Club, Philadelphia, Thursday, March 16th. The program consisted of a lecture on "Magnetism," by Dr. Edward A. Partridge, professor of physics, Central Manual School, Philadelphia, Pa. The lecture was illustrated by lecture-table experiments and lantern slides, and among the subjects discussed were the following: Brief History; Theory of Magnetism; Zeeman Effect and Sun Spots; Mechanical and Chemical Relations of Sun Spots; Magnetic Phenomena in Alloys of Non-Magnetic Metals. C. S. BRINTON, *Secretary.*

WISCONSIN SECTION.

The March meeting was held jointly with the W. W. Daniells Club, at Madison, on Thursday, March 16th, at 8 P.M., in the Auditorium of the Chemistry Building. The address of the evening was on "The Manufacture of Artificial Carbon Products," by B. Dyer, of the National Carbon Company.

The April meeting was held at Madison, on Wednesday, April 5th, at 8 P.M., in Room 113 of the Chemistry Building. Addresses were given by O. E. Ruhoff, formerly superintendent of the Acid Dept., Mineral Point Zinc Co., on "Some Problems Encountered in the Manufacture of Sulfuric Acid by the Contact Process," and by H. G. Deming, on "Some New Solvents for Cellulose." W. G. WILCOX, *Retiring Secretary.*

CHICAGO SECTION.

The March meeting was held in the rooms of the Western Society of Engineers, on Friday evening, March 17th, at 8 P.M., following the usual informal dinner. The general subject of the evening was "Ore Deposits," and the following papers were read and discussed: "The Conservation of Ore Deposits," Prof. Rollin D. Salisbury, University of Chicago. "The Chemistry of Enrichment of Gold, Silver and Copper Ores," Prof. W. H. Emmons, University of Chicago.

The April meeting was held in the rooms of the Western Society of

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Engineers, on Friday evening, April 14th, at 8 P.M., preceded by an informal dinner.

The general subject of the evening was "Sugar Manufacture," with papers on "The McMullen Process of Sugar Manufacture," by Prof. Harry McCormack, Armour Institute, and "Cellulose," by Earle W. McMullen, Armour Institute. General discussion followed.

D. K. FRENCH, *Secretary.*

LOUISIANA SECTION.

The forty-eighth meeting was held at the Directors' Room of the Board of Trade, New Orleans, Friday, March 17th, at 8 P.M.

The following program was presented. "The Volumetric Determination of Phosphoric Acid," by Dr. Chas. E. Coates and Mr. A. P. Kerr. "A Chemical Study of Louisiana Cypress," by Dr. Allan F. Odell. A Dutch supper was served in the meeting room immediately after the reading of the papers.

GEO. B. TAYLOR, *Secretary.*

MINNESOTA SECTION.

The 32nd regular meeting was held Friday evening, March 17th, in the Chemical Laboratory of the University of Minnesota, with fifty-eight in attendance. Mr. Brainerd Dyer, of the National Carbon Co., gave an illustrated lecture showing the process of manufacturing amorphous carbon electrodes. At the close of the lecture Mr. Dyer was given a unanimous vote of thanks for his very interesting lecture.

FRANCIS C. FRARY, *Secretary.*

NEW YORK SECTION.

An extraordinary meeting was held on the evening of March 17th as a part of the exercises at the opening of the Chemists' Building.

The program was as follows: Address by the Chairman of the Section, Chas. Baskerville. "The Characteristics of Living Matter from the Physico-chemical View-point," by Jaques Loeb. "The Rare Gases of the Atmosphere," by R. B. Moore.

The seventh regular meeting of the session of 1910–'11 was held at Rumford Hall in conjunction with the American Electrochemical Society on April 7th.

The program was as follows: "Suggestions as to Public Safety," by C. F. McKenna. Discussed by Wm. Jay Schieffelin and G. W. Thompson. Presidential address, "Chemical Research and Industrial Progress," by William H. Walker. "The Relation of Surface Tension to Electrochemical Action," by Harrison E. Patten.

C. M. JOYCE, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The thirty-ninth meeting was held on March 22nd. Mr. Brainerd Dyer, of the National Carbon Company, gave an illustrated lecture on "The Carbon Industry."

GRINNELL JONES, *Secretary.*

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UNIVERSITY OF MICHIGAN SECTION.

The March meeting was held Wednesday, March 22nd, at 8 P.M., in the Chemistry Building, with twenty-four members in attendance. The following papers were presented: "The Citro-compounds of Iron," by A. B. Stevens. "The Molecular Weight and Other Properties of Sulfur Trioxide," by D. M. Lichty.

WM. GABB SMEATON, *Secretary.*

KANSAS CITY SECTION.

A sectional meeting was held Saturday, March 25th, at Lawrence, at the University, beginning at 5 o'clock, followed by dinner at 6.30. The program was as follows: "Observations on the Teter Point of Mixed Fatty Acids," by William J. Reese, chemist for Peet Bros. Manufacturing Co. "The Laboratory and the Packing Plant," by Lyman S. Bushnell, chief chemist for Armour Packing Co.

E. A. WHITE, *Secretary.*

MILWAUKEE SECTION.

A regular meeting of the Section was held on Friday evening, March 31st, at the Hotel Blatz. An address on "The Utility of the Metallographic Microscope in Engineering Practice" was given by Prof. James Aston, of the University of Wisconsin. The usual informal dinner preceded the meeting.

BEN L. SALOMON, *Secretary.*

EASTERN NEW YORK SECTION.

The regular meeting for April was held at the Bender Laboratory in Albany on Friday evening, April 7th, at 8 o'clock.

The topics of the evening were: "Certain Phases of Immunity," by Dr. Thomas Ordway, with demonstrations by Dr. H. S. Bernstein, and "The Chemical and Physiological Importance of the Nuclei Acids and their Cleavage Products," by Dr. Victor C. Myers.

G. R. FONDA, *Secretary.*

LOUISVILLE SECTION.

The April meeting was held in Louisville on the 8th, with about thirty present. The Lexington members were the guests of the Louisville members for the day. Visits were made to the Frank Fuhr Brewery and the J. B. Speed Cement Plant. Dinner was served at the Galt House in the evening. The following officers were elected for the ensuing year: *President*, R. C. Lord; *First Vice-President*, A. M. Peter; *Second Vice-President*, C. E. Martin; *Secretary*, Karl S. Markendorf, 441 E. Broadway, Louisville, Ky.; *Treasurer*, B. M. Overton; *Councilor*, R. M. Parks.

F. F. HASBROUCK, *Retiring Secretary.*

CONNECTICUT VALLEY SECTION.

The Section held its first meeting for purposes of organization on Saturday evening, April 8th, at the Chemical Lecture Room of Trinity College, Hartford. The Secretary of the Society, Charles L. Parsons, was present and presided.

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Dr. Edward W. Morley addressed the Section on "The Work of the Eighth Congress." Charles L. Parsons spoke on "The Value of Research Laboratories to the American Chemical Industries." Prof. Walter P. Bradley and Mr. F. W. Farrell also addressed the meeting.

The following officers for 1911 were elected: *Honorary Chairman*, E. W. Morley; *Chairman*, F. W. Farrell; *Vice-Chairman*, R. B. Riggs; *Secretary-Treasurer*, Warren I. Keeler, 214 Main St., New Britain, Conn.; *Councilor*, R. R. Renshaw.

WARREN I. KEELER, *Secretary.*

CLEVELAND SECTION.

The April meeting was held in Morley Laboratory, Adelbert College, Western Reserve University, on Monday evening, April 10th, at 8 P.M.

The laboratory was open for inspection during the evening.

Professor Tower gave an illustrated lecture on "The Properties of Solutions." After the lecture a complimentary luncheon was served by the university.

W. R. VEAZEY, *Secretary.*

CINCINNATI SECTION.

The 168th regular meeting of the Section was held on Wednesday evening, April 12th, at the Ohio Mechanics Institute, at 8 P.M.

The paper for the evening, entitled "A New Element, or the Decay of an Element," was given by Dr. Chas. T. P. Fennel, of the Cincinnati College of Pharmacy.

The Executive Committee reported on the changes for the Constitution.

ALFRED SMITH, *Recording Secretary.*

WASHINGTON SECTION.

The 206th meeting was held at the Cosmos Club, Thursday, April 13th, at 8 P.M.

The program was as follows: "The Cost of Manufacturing Illuminating Gas" (from the Chemical Engineer's Standpoint), by Chas. E. Munroe. "Chenopodium Oil," by E. K. Nelson. "The Phenomenon of Occlusion by Precipitates of Barium Sulfate," by John Johnston and L. H. Adams.

H. S. BAILEY, *Secretary.*

DECEASED MEMBER.

Mrs. Ellen H. Richards, March 30, 1911, Massachusetts Institute of Technology, Boston, Mass.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 186.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. IV. THE STANDARDIZATION OF A TIP; AND THE CALCULATION OF THE SURFACE TENSION AND MOLECULAR WEIGHT OF A LIQUID FROM THE WEIGHT OF ITS FALLING DROP.

BY J. LIVINGSTON R. MORGAN.

Received March 8, 1911.

After determining, as described in the previous paper,[1] the average weight of a drop of liquid *falling of its own weight alone* from the tip, using for the purpose at least three checking values each, of the 30 drops, and of the 5-drop blank, the next step is to find the constant, of the tip, *i. e.*, the temperature coefficient of the molecular function, $w(M/d)^{2/3}$.

In the previous papers of the series,[2] the method employed to this end was the one first used, for surface tension from capillary rise, by Ramsay and Shields,[3] and since then by all other investigators in that field. This method consists in evaluating k in the equation[4]

[1] Morgan, THIS JOURNAL, 33, 349–362 (1911).

[2] I. Morgan and Stevenson, THIS JOURNAL, 30, 360 (1908). II. Morgan and Higgins, *Ibid.*, 30, 1055 (1908).

[3] *Z. physik. Chem.*, 12, 431 (1893).

[4] Here γ is the surface tension in dynes per centimeter, d the density, both at the temperature of observation t, M is the molecular weight as a liquid, k for non-associated liquids is a constant which is assumed to be universal and equal to 2.12 ergs, and t_c is the critical temperature.

This law, of course, can also be expressed in the form of a proportion, in which case the arbitrary constant, 6, disappears. We have then for any two non-associated liquids

$$\gamma'(M'/d')^{2/3} : \gamma''(M''/d'')^{2/3} :: (t'_c - t') : (t''_c - t'');$$

in other words, *at temperatures equally removed from the critical temperature* (*i. e., in corresponding states*), *the value of the expression* $\gamma(M/d)^{2/3}$ *is identical for all non-associated liquids.*

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$$\gamma_1(M/d_1)^{2/3} = k(t_c - t_1 - 6) \quad (1)$$

by aid of the second, differential, equation

$$\frac{\gamma_1(M/d_1)^{2/3} - \gamma_2(M/d_2)^{2/3}}{t_2 - t_1} = k, \quad (2)$$

the molecular weight of the substance as a liquid being estimated by the relationship of this value of k to that found in the same way for some other liquid, taken as a standard; or to the average value of k found for several such. The results thus obtained from capillary rise can hardly be considered as satisfactory, for the k values so calculated are found to vary considerably from the mean and to force the conclusion that most substances in the liquid state are either slightly associated (*e. g.*, aniline, $k = 2.01–2.053$, and pyridine, $k = 2.07$), or slightly dissociated (quinoline, $k = 2.21–2.44$), if we can conceive of such a process in a pure liquid.

This value of k, as calculated from (2) for any liquid, was then supposed to be substituted in (1) to obtain the critical temperature of that liquid; but, as Dutoit and Friederich[1] have already observed, the agreement of these values found from capillary rise results with those obtained directly is so unsatisfactory (aniline, quinoline and pyridine, etc.) that the relationship is not of very great value for the calculation of critical temperature.

A glance at equation (2) shows at least one possible cause for much of the variation in the value of k calculated for the various substances from (2), viz., the error induced in k by a known error in one of the experimental results. Thus *when calculated from* (2), *the percentage error in k is equal, not to the original, experimental, error, but to that multiplied by a factor which is the greater, the smaller the temperature interval* $t_2 - t_1$, for the actual error in the value of $\gamma(M/d_1)^{2/3}$ is then carried over bodily to the difference $\gamma_1(M/d_1)^{2/3} - \gamma_2(M/d_2)^{2/3}$, which may be but one-tenth or one-twentieth, or even a smaller fraction, of $\gamma_1(M/d_1)^{2/3}$, in which case *the percentage error in the difference, and consequently also in k, will be ten or twenty or even more times that of the original observation.* This error, naturally, will be increased or decreased by an error in $\gamma_2(M/d_2)^{2/3}$, according as that has the opposit or the same sign as the one in $\gamma_1(M/d_1)^{2/3}$; and further will be influenced by the relation of the error in $t_2 - t_1$ to that in t_1, or in t_2.

The recognition and attempted elimination of this error, by making $t_2 - t_1$ as large as possible, in place of obviating the difficulty, often simply increases it. This is the case with liquids of high viscosity, which, especially when accompanied by low density, makes the measured ascensions in a capillary of very small bore probably erroneous at low temperatures, while at the higher ones, that difficulty being partially or wholly eliminated, only the error due to the small height to be measured, which may also be

[1] *Arch. sci. phys. Genève*, 9, 128 (1900).

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considerable, is present. It is in this respect that the drop weight method has a decided advantage over that of capillary rise as a means of determining surface tension, for with the new form of apparatus the error which may exist can be retained constant (which is the important thing) by weighing a larger number of drops at the higher temperatures, and errors due to changing viscosity are not present. The absence of these errors is also clearly shown in the work of Morgan and Higgins (on the older form of apparatus), who find k values from their extreme values of drop weight, even by aid of (2), for aniline, pyridine and quinoline which are practically identical with those for the other three liquids, benzene, chlorobenzene, and carbon tetrachloride. This is in startling contrast to the results from capillary rise given above.

We can conclude from the above, then, that in calculating k from equation (2) in the customary way, even small irregular, experimental errors (and in capillary rise it must be conceded that these are rarely absent) will become so largely magnified at times as to make the results absolutely meaningless, if not wholly misleading, while in all cases the variation in the calculated value of k from (2) will cause even those experimental results which are exceedingly accurate to appear but mediocre[1].

To avoid this error in the calculation of k from (2) (both for drop weight and capillary rise), so that results on the new form of apparatus can be compared directly with the results obtained from capillary rise, and a new tip standardized as quickly and accurately as possible, another method for the calculation of k has been resorted to with a very satisfactory result. If equation (1) be true, *i. e.*, if the value of the function $\gamma_1(M/d_1)^{2/3}$ is the same for all non-associated liquids at corresponding temperatures; in other words, is simply a function of the reduced temperature $(t_c - t_1 - 6)$ the value of the molecular temperature coefficient k, calculated from (1), with the known critical temperature, for any one liquid, should lead to the correct critical temperature of any other such liquid when its data (*i. e.*, w, M and d) are substituted with this value of k in (1). From a series of results for any one, standard liquid, then, using the known value of t_c, we would get as many values of k as there are individual results, and could find an average value which when substituted in (1) would give the variation of the value of the function $\gamma(M/d)^{2/3}$, with the temperature, for that liquid, and for all other normal ones, up to 6° below the critical temperature, when its value would become zero.

Naturally, if there were no experimental error, this value of k would be identical with that found by aid of (2). *When any error at all exists,*

[1] This is shown by the intermediate values of k found in this way by Morgan and Higgins, where the greatest variable experimental error is not greater than a few hundredths of one per cent.

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however, here, in contrast to the method based upon (2), the percentage error in k will be the same as that in the original, experimental, result itself.

In case this value of k, determined in average for any one standard liquid of known critical temperature, is now substituted in (1) with the data for another non-associated liquid, the value of its calculated t_c should be the same (within the percentage error existing in the experimental work), no matter what the temperature, t, may be; and the mean of these individual values, provided the law (1) is correct, should agree closely with the observed critical temperature of that liquid. Here, when the result at one temperature differs from those at the others, it would point to an unsuspected error, and that value should be scrutinized carefully before including it in the average result.

It is this method which has been selected for the standardization of a tip, benzene ($t_c = 288.5°$) being employed as the standard liquid. In addition to its use as a means of calculating the molecular temperature coefficient k, it can also serve for the calculation of the factor necessary to transform the drop weight from any tip directly into surface tension; and for the direct comparison of the surface tension results of various observers, even though the determinations were not made at the same temperatures.

In Table I are given the k values which are necessary in equation (1), with capillary rise as well as drop weight results, to give benzene its observed critical temperature of 288.5° C.

TABLE I.

Benzene, $t_c = 288.5°$; M = 78.

t.	d.	γ.	$\gamma (M/d)^{2/3}$.	k from (1).
		Renard and Guye.[1]		
11.4	0.888	28.83	569.68	2.1014
31.2	0.867	26.68	535.68	2.1316
55.1	0.842	23.53	481.74	2.1185
68.5	0.827	21.70	449.63	2.1011
78.3	0.815	20.51	429.13	2.1015
			Average,	2.1108
		Ramsay and Shields.[2]		
80	...	...	425.1	2.0948
90	...	...	404.5	2.1013
100	...	...	384.0	2.1041
110	...	...	362.9	2.1038
120	...	...	341.6	2.1022
			Average,	2.1012

[1] *J. chim. phys.*, 5, 81 (1907). Capillary rise in presence of air. Results of $\gamma(M/d)^{2/3}$ recalculated throughout to give uniformity.

[2] *Loc. cit.* Capillary rise, absence of air.

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t.	d.	γ.	$\gamma(M/d)^{2/3}$.	k from (1).
		Ramsay and Aston.[1]		
11.2	0.8871	29.21	575.6	2.1216
46.0	0.8500	24.71	502.3	2.1239
78.0	0.8147	20.70	433.1	2.1179
				Average, 2.1211
		Morgan and Higgins.[2]		
11.4	0.888	35.239	696.32	2.5685
30.2	0.868	32.350	649.02	2.5724
53.2	0.844	28.866	590.05	2.5710
68.5	0.827	26.530	549.71	2.5687
				Average, 2.5702

A comparison of these average values of the k necessary to give $t_c = 288.5°$ shows that even though Renard and Guye worked in the presence of air (as did Morgan and Higgins), their results differ less from those in the absence of air of Ramsay and Shields, than do those of Ramsay and Aston, who also excluded air. Except when the liquid dissolves considerable air, then, we should except identical results with and without the presence of air.

These k values at the various temperatures also seem to agree better in the case of drop weight than in that of capillary rise. This is to be expected, however, especially with the new form of apparatus, for the smaller weight of a single drop at the higher temperatures can be compensated by increasing the total number weighed, while with the capillary rise method, even the originally small height of ascension decreases with the increase in temperature, and causes an increase in the percentage error.

In using for any one liquid the equation

$$\gamma(M/d)^{2/3} = k(t_c - t - 6)$$

as a means of comparison at any one temperature, since M, t_c, t and d are all taken as the same, it is clear that γ in each case must be proportional to its value of k. We have, then, for the results of different observers, *at the same temperature*,

$$\gamma_1 : \gamma_2 :: k_1 : k_2, \qquad (3)$$

where γ_1 and γ_2 are the surface tensions of benzene that would be found at this temperature by different observers, whose average constants for benzene at other temperatures are k_1 and k_2. This holds, naturally, also for the comparison of drop weights and surface tensions, where we have, *also at the same temperature*,

$$w : \gamma :: K : k, \qquad (4)$$

[1] *Z. physik. chem.*, 15, 91 (1894). Same conditions as Ramsay and Shields.
[2] *Loc. cit.* Drop weights.

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w being the weight in milligrams, and K the constant for drop weight, calculated similarly to k.

Since, further, the ratio of γ for benzene to γ for any other liquid still at the same temperature, as found by one observer must be the same, within the limits of error, as that found under similar conditions by every other observer, it is apparent that

$$\gamma_B/\gamma_x = \gamma'_B/\gamma'_x,$$

where γ_x and γ'_x are the respective values found by two of the observers for the second liquid *still at the same temperature.* Combining this equation with the proportions (3) and (4), remembering that these ratios must also be equal to w_B/w_x under identical conditions of temperature we find

$$\gamma_x : \gamma'_x : : k : k'$$

and

$$w_x : \gamma_x : : K : k,$$

i. e., the surface tensions of the same liquid, x, at the same temperature, as would be found by different investigators, are proportional to the average k values of benzene found by them; and

The drop weight in milligrams of any liquid is related to its surface tension, in dynes per centimeter, at the same temperature, as the K value for that tip is to the k value of surface tension, both being found from benzene by aid of (1), *using* $t_c = 288.5°$.

The relationship of drop weight to surface tension, *both at the same temperature,* can be found, then, from the equation

$$\gamma_{\text{dynes}} = w_{\text{mg.}} \times k/K, \qquad (5)$$

where, since the constants, k, of the three observers do not agree very satisfactorily, it would be best perhaps to use for K the average of their values. We would have thus for the tip used by Morgan and Higgins, the equation of transformation

$$\gamma_{\text{dynes}} = w_{\text{mg.}}\ 2.1110/2.5702 = 0.82134\ w_{\text{mg.}}.$$

In place of calculating by the above relations all the γ and w values to one γ form, to compare the work on other liquids by the various observers (in which case the temperatures would have to be identical), we can more simply attain the desired end in another way, retaining the above average values, $k_{R\&G}$, $k_{R\&S}$, $k_{R\&A}$, and $k_{M\&H}$.

Since in comparing the results of the various observers on any one new liquid, at various temperatures, by aid of equation (1) and the normal constant k, the value taken for M would be the same, and d would be the same function of the temperature in all, while in every case, at the same temperature, γ would be proportional to its value of k, it is clear that *when the normal k (i. e., that value found for benzene) is also the real and correct molecular temperature coefficient of the new liquid, the same value*

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of t_c (within the experimental error) will be found from all temperatures, not only from the results of one observer, but also independent of the origin of the results. A constant value of the calculated t_c at all temperatures, then, indicates that the normal molecular temperature coefficient k_0 for benzene is also the correct one for this liquid, and that consequently, the liquid is non-associated, notwithstanding the misleading value of k which might be found from equation (2).

We find then from the above, not only a new definition of normal molecular weight in the liquid state, but also a method of comparing results of surface tension of any liquid, at different temperatures, among themselves, or with drop weights, for the constant t_c calculated in each case for the liquid from the normal specific benzene value of k should always be the same, within the limits of errors, according to the results of all observers.

The above result may also be expressed graphically by plotting the change of the function $w(M/d)^{2/3}$ with the temperature. Here the values of t from 0° up are laid out on the vertical axis, those of $w(M/d)^{2/3}$ being reckoned from 0 up, *to the left*, on the horizontal axis, the temperature axis intersecting that of $w(M/d)^{2/3}$ at the value of $w(M/d)^{2/3} = 0$. The line representing the mean value for benzene begins at 0°, where $w(M/d)^{2/3}$ is large and runs to the right, ending where it intersects the temperature axis at the point t_c—6 (*i. e.*, at 288.5 —6°), where its value becomes zero. Locating the observed point $w(M/d)^{2/3}$ for any new non-associated liquid, at its proper temperature, and drawing through it a line parallel to that for benzene, *i. e.*, of the same slope k, we find, where it intersects the temperature axis, its value of t_c—6. Repeating this operation for other points, *i. e.*, at other temperatures for the same liquid, we get a series of parallel lines, each leading to a value of t_c—6. The mean of these values, provided the difference is within the limits of error, is then the correct value of t_c—6; *and the slope k, i. e., the value for benzene which was used is the correct one for that liquid, which must consequently also be non-associated.*

In Tables II–VI are grouped together the values of t_c as calculated in the above way from the drop weights and surface tensions from capillary rise of aniline, carbon tetrachloride, chlorobenzene, pyridine and quinoline, using in each case the value of k found above for benzene, where $t_c = 288.5°$.

TABLE II.—ANILINE, M = 93, t_c = 426.
Renard and Guye, k_B = 2.1108.

t.	d.	r.	$r(M/d)^{2/3}$.	t_c calc. from (1).
10.2	1.026	42.60	859.61	423.4
30.1	1.010	40.71	830.13	429.4
54.5	0.990	37.92	783.61	431.6
66.0	0.979	36.24	754.49	429.4

Average, 428.05

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t.	d.	γ.	$\gamma(M/d)^{2/3}$.	t_c calc. from (1).
	Dutoit and Friederich,[1] $k_B = 2.1012$.			
19.5	1.018	40.84	827.0	419.1
44.4	0.999	38.36	787.8	425.3
77.7	0.970	35.06	734.6	433.3
			Average,	425.9°
	Ramsay and Shields, $k_B = 2.1012$.			
132.1	0.9212	30.23	655.4	450.0
184.5	0.8720	24.36	547.8	451.2
	Morgan and Higgins, $k_B = 2.5702$.			
29.0	1.0138	49.362	1004.03	425.7
51.7	0.9944	45.902	945.76	425.7
67.1	0.9810	43.588	906.24	425.7

TABLE III.—CARBON TETRACHLORIDE, M = 153.8, t_c = 283.2.

	Ramsay and Shields.			
80	...	...	414.6	283.2
100	...	...	372.3	283.2
	Ramsay and Aston, $k_B = 2.1211$.			
11.8	...	...	565.7	284.5
46.0	...	...	492.6	284.2
78.0	...	...	426.3	285.0
			Average,	284.6°
	Renard and Guye.			
11.8	1.610	26.93	562.76	284.4
23.8	1.587	25.74	543.08	287.1
33.0	1.569	24.60	522.99	286.8
44.5	1.546	23.21	498.32	286.6
55.3	1.525	21.97	476.01	286.8
68.0	1.500	20.38	446.46	285.5
			Average,	286.2°
	Morgan and Higgins.[2]			
24.2	1.5823	30.981	645.946	285.0
54.0	1.5240	26.685	578.397	285.1

TABLE IV.—CHLOROBENZENE, M = 112.5, t_c = 360.

	Ramsay and Shields.			
150	...	...	423.2	357.4
180	...	...	360.5	357.6
200	...	...	319.1	357.9
			Average,	357.6°

[1] *Arch. sci. phys. nat.*, 9, 105 (1900).

[2] Later work with the simple form of apparatus, with a tip of 4.5 mm., where the control is perfect leads to a result for this liquid of 283.1°, which makes it appear that here on this large tip (6.2 mm.), even with long tail of liquid in the buret the drop did not fall of its own weight alone; this will be discussed in a later paper.

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t.	d.	r.	$r(M/d)^{2/3}$.	t_c calc. from (1).
		Ramsay and Aston.		
9.5	1.1182	33.71	729.1	359.2
45.6	1.0795	29.30	648.8	357.5
77.8	1.0444	25.66	581.0	357.7
131.3	0.9836	19.93	469.8	357.8
			Average,	358.1°
		Renard and Guye.		
10.7	1.117	33.47	724.53	359.9
39.0	1.087	29.83	657.06	356.3
50.8	1.073	28.49	633.47	356.9
64.0	1.059	27.02	606.07	357.1
73.8	1.048	25.99	587.04	357.1
86.0	1.034	24.67	562.70	358.6
100.0	1.017	23.16	533.70	358.8
119.3	0.993	21.04	492.62	358.7
126.9	0.985	20.30	477.87	358.3
			Average,	358.2°
		Morgan and Higgins.		
8.2	1.1200	41.082	887.717	359.6
39.2	1.0856	36.628	808.106	359.6
50.8	1.0730	34.990	778.000	359.5
63.9	1.0590	32.200	744.690	359.7
72.2	1.0498	32.054	723.180	359.6

TABLE V.—PYRIDINE, M = 79, t_c = 344.2°.

		Renard and Guye.		
10.5	0.991	36.67	679.22	338.3
39.2	0.963	33.58	633.99	345.6
58.8	0.943	30.48	583.57	335.0
74.2	0.927	28.32	548.44	340.0
91.1	0.911	26.16	512.52	345.6
108.2	0.894	24.19	479.91	341.6
			Average,	341.0°
		Ramsay and Shields.		
17.0	0.9825	38.40	715.3	362.8
46.2	0.9512	34.17	650.3	360.7
		Dutoit and Friederich.		
17.5	0.985	36.69	682.7	348.4
56.3	0.946	30.86	589.6	342.9
78.6	0.923	28.53	554.0	348.3
91.0	0.911	26.54	521.1	345.0
			Average,	346.2
		Morgan and Higgins.		
10.5	0.991	45.804	848.401	346.6
39.2	0.962	40.980	774.236	346.4
58.8	0.943	38.000	727.546	347.9[1]
74.2	0.927	35.370	684.962	346.7

[1] Error due to lack of stirring of bath; see original paper.

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TABLE VI.—QUINOLINE, M = 129, t_c = <520°.

t.	d.	r.	$r(M/d)^{2/3}$.	t_c calc. from (1).
		Ramsay and Shields.		
15.4	1.098	45.13	1082.0	536.3
78.4	1.044	37.44	928.7	526.4
		Bolle and Guye,[1] k_B = 2.1011.		
10.5	1.1013	41.34	1054.6	518.4
57.6	1.0641	40.10	982.1	531.0
108.2	1.0233	34.36	863.8	525.3
149.8	0.9299	28.24	756.9	515.0
			Average,	522.4°
		Renard and Guye.[2]		
8.2	1.103	44.71	1069.27	520.8
31.0	1.084	41.97	1015.42	517.1
55.0	1.066	39.35	962.96	517.2
65.2	1.058	38.20	939.29	516.0
80.5	1.046	36.50	904.34	514.9
98.0	1.032	34.71	867.75	515.1
			Average,	516.9°
		Morgan and Higgins.		
30.7	1.0852	51.525	1245.68	521.4
55.0	1.0658	48.344	1182.91	521.3
65.0	1.0576	47.053	1157.27	521.3[3]

A glance at the t_c values calculated from the capillary rise results for the five additional liquids, using for all the normal change per degree in the value of the function $w(M/d)^{2/3}$, as found for benzene, will serve to show that in general there is either no decided trend in the values for any one case, or that if there is such a trend it is negatived by either an opposit trend, or no trend at all, in the work of one of the other observers; and that throughout the average results from drop weight agree (within a reasonable error) with those of the others. As far as concerns aniline, it is true that the absence of trend is shown only by Renard and Guye, whose results at 66° is the same as that at 30.1°, although the value between them is larger; but this irregularity certainly shows the possibility of an error as high as 0.5 per cent., at any rate. It must be remembered here, however, that aniline, in addition to its high viscosity, is characterized by its extreme stickiness, which is so persistent that the traces of liquid can be removed from a tube only by aid of some solvent; the combination of these two properties, consequently, would make the re-

[1] *J. Chim. Phys.*, 3, 40 (1905).

[2] The authors here used Kahlbaum's quinoline, without redistilling it. With drop weight the preparation which contains water always gives a result about 1 per cent. too low in value, *i. e.*, about 516° for t_c. It is always to be redistilled just before using.

[3] By an error in the original paper this read 68° in place of 65°.

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sults for aniline, more than for any other liquid, open to suspicion in any method depending upon the position assumed by a column in a fine capillary tube when it is drawn above its normal position, and then allowed to settle into it. Even with the drop weight method, the greatest care must be exercized to keep this liquid out of the capillary before the liquid for the first drop is allowed to run over, for otherwise the liquid which adheres will be formed into threads and forced out ahead of the drop; and between determinations the dropping tube must be cleansed out with ether and dried.

The results of Ramsay and Shields for aniline, pyridine, and quinoline are probably incorrect, as they disagree with the results of the other investigators, using the same method. That in the case of aniline the high t_c found by them is not simply the result of the trend is shown by the fact that Renard and Guye at 175°, *i. e.*, a temperature lying between those of Ramsay and Shields find a value of only 436.8° (as against their 450°) which is little more than 1 per cent. larger than the value at 54.5°.

When it is remembered, further, that the results by drop weight are so free from variable error that the k for benzene from (1), as used above, has practically the same value as that found for all the liquids by (2), where the k values from capillary rise as calculated from (2) varies for all irregularly and in a meaningless way, *we must concede that this method of finding k from* (1) *justifies the conclusion that all these liquids not only by drop weight, but also capillary rise, are absolutely non-associated, i. e., have the same molecular temperature coefficient of surface tension, as has benzene which is taken as a standard, notwithstanding the meaningless values of k found (from capillary rise) by equation* (2), *which vary from 1.88 to 2.44 in place of the assumed normal value 2.12.*

It has been shown by Walden[1] that the critical temperature of a liquid can also be found from surface tension by a method which does not necessitate a knowledge of its molecular weight. This method is based upon a knowledge of the temperature coefficient of surface tension and that of the capillary constant. Since the drop weight is proportional to the surface tension and the drop volume ($v = w/d$) to the capillary constant, this method must also be applicable to the drop results above. Walden's values of α' and α'' should then be given by the equations

$$w_t = w_o(1-\alpha' t) \text{ and } v_t = v_o(1-\alpha'' t).$$

The values of α' and α'' should be approximately proportional inversely to the critical temperature in such a way that a variation in one is compensated by the opposit variation in the other, so that the mean leads to the correct critical temperature.

By combining the two relationships

[1] *Z. physik. Chem.*, 65, 175 (1908).

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$$\alpha' \times a = t'_c \text{ and } \alpha'' \times b = t''_c,$$

remembering that $\frac{t_c' + t_c''}{2} = t_c$, where a and b are constants, we find

$$t_c = \text{constant } \frac{\alpha' + \alpha''}{\alpha'\alpha''}. \qquad (6)$$

It will be noted here, of course, that the α' and α'' values are susceptible to the same error that k by (2) is, but notwithstanding this (6) should lead, if the relationship is correct, to practically the same values of t_c found above, when the value of the constant is found for benzene. The values of α' and α'' found for drop weight should, of course, be the same as those calculated for surface tension, for they represent only a percentage change per degree in the property. In Table VII are given these values, as found from the drop weights of Morgan and Higgins, as well as those found by Walden from the mean of all the results of surface tension from capillary rise, together with the values of t_c as calculated for each.

TABLE VII.[1]

	Drop weight.			Surface tension.		
Liquid.	α'.	α''.	tc.	α'.	α''.	t_c.
Benzene	0.004130	0.003231	[288.5]	0.00416	0.00329	288.5°
Aniline	0.002819	0.002167	426.9	0.00261	0.00208	448
Carbon tetrachloride	0.004182	0.003268	285.1	0.00418	0.00337	279
Chlorobenzene	0.003339	0.002565	360.5	0.00311	0.00266	363
Pyridine	0.003447	0.002661	348.3	...	0.00258	..
Quinoline	0.002347	0.001738	523.8	0.00260[2]	0.00196	..

It is quite clear from the above that this empirical relationship holds better for drop weight than it does for capillary rise, as a means of calculating t_c independently of the molecular weight. If the variation in calculated t_c by equation (1) is large, the value calculated by (6) will depend upon whether the t_c from (1) increases or decreases with the temperature.

It will be noted from the tables that the values calculated for t_c from k_B agree satisfactorily for the liquids considered with the values of critical temperature observed directly. A survey of the literature, however, shows that this is not always the case, although it appears at present as if enough liquids giving the observed value of the critical temperature, with the normal constant k, will be gained, such as pyridine, aniline, and quinoline, to compensate for those which by this method of calculation will give a differing value, but which by a combination of errors gave with the k of (2) the correct value.

[1] The (benzene) constant for drop weight in (6) is 0.52299, from which the other values of tc are calculated. The values of Walden are those given by him, using an average constant.

[2] From Ramsay and Shields only.

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The great gain by this point of view, however, *is the possibility that by it we may simplify the definition of the normal molecular weight of substances in the liquid state*, which at present is in an extremely unsatisfactory form. It would seem as if the following three important classes of liquids can be distinguished:

I. Those liquids for which the normal (benzene) value of k leads in equation (1) to a value of t_c which agrees closely with the observed value of the critical temperature, at all temperatures.

II. Those liquids for which the normal (benzene) value of k leads in equation (1) to the same calculated value of t_c (within a reasonable error), at all temperatures, but which differs from the observed critical temperature; in some cases, considerably.

III. Those liquids which with the normal (benzene) value of k lead to a calculated value of t_c which is not only lower than that observed, but which increases with an increase in the temperature of observation. This is the typical case of an associated liquid (water, ethyl alcohol, methyl alcohol, and acetic acid) where $w(M/d)^{2/3}$ is not a linear, but a curvilinear, function of the temperature. The true critical temperature can be found in this case by first obtaining the equation of the curve, as has already been done by Morgan.[1]

In cases I and II the liquids are non-associated, *i. e.*, the normal molecular temperature coefficient leads to a satisfactory, constant, value of the term t_c. Case II here would differ from I only that the function does *not become zero at 6 degrees below the observed critical temperature*, but *6 degrees below another, fictitious, temperature*—in other words, the conditions of corresponding states (as judged by the distance from the critical temperature) are fulfilled for those liquids in class I, but for an unknown reason are not fulfilled for those in II.

All these cases, together with the anomalous malic esters, which lead in (2) to a k value greater than 3, as well as water solutions, are now being studied in this laboratory by the drop weight method, and will be discussed as the results are reported.

Of the application of this point of view to the very recent work of Walden[2] on tripalmitin and tristearin, which by (2) give a k value of from 5 to 6, it may be said that using the normal k value of 2.126, as calculated from his results for benzene, it is found that the trend downward in the calculated value of t_c amounts to roughly 7–8 per cent. When we consider here that the difference in the height of ascension between 57.7° and 134.7° is but 0.455 cm. (*i. e.*, from 3.017–3.472) for one, and but 0.4 cm. (*i. e.*, from 3.012–3.412) for the other between 33.7° and 125.1°; and that at 90° the viscosity of tripalmitin is equal to, and that of tri-

[1] THIS JOURNAL, 31, 309 (1909).

[2] *Z. physik. Chem.*, 75, 555 (1910).

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stearin, at the same temperature, is 1.18 times, the viscosity of a 40 per cent. sugar solution at 0°, and the density is 0.84–0.89, while the bore of the capillary tube is but 0.0193 cm., it is perhaps more logical to assume that possibly an unrecognized error exists to the extent of from 7 to 8 per cent. in one of the extremes, rather than to conclude that the liquids are dissociated in an unknown way to such an extent that 5 moles are produced from every one originally present. At any rate until the results are carried to higher temperatures, and precautions taken to eliminate the possibility of the above errors, we can hardly consider these liquids as belonging to a new group, as perhaps the liquefied gases, which give low, but constant, values of k, may. It is to be remembered here that no claim is made that all liquids must be included in these classes, although it is quite certain that by this point of view a very large number of liquids, hitherto regarded as anomalous in their behavior, will be proven to be perfectly normal.

It was at first intended to include in this paper a discussion of the relationships existing between drop weight and the various other physical constants of a liquid, but it was thought best to defer that until a larger number of results had been reported upon. It will consequently form the subject of a later paper.

The results of this paper may be summarized as follows:

I. A method is presented for standardizing a tip, *i. e.*, for finding the normal molecular temperature coefficient, k, of all the non-associated liquids falling from it, which is based solely upon the equation $w(M/d)^{2/3} = k(t_c - t - 6)$, and does not make use of the differentiated form of Ramsay and Shields for results from capillary rise, *viz.*: $\Delta[w(M/d)^{2/3}]/\Delta t = k$, with its customary multiplication of the experimental error.

II. It is then shown that the surface tension in dynes of any liquid at any temperature can be calculated from its drop weight in milligrams from any tip at that temperature by multiplying the latter by the ratio of the k value of surface tension, to the k value for that tip, both being found by use of benzene ($t_c = 288.5°$) as the standard.

III. Any liquid which, with this normal (benzene) value of k, gives the same calculated value of t_c, within the limits of error, at all the temperatures of observation, is then to be regarded as a normal non-associated liquid, for this proves that the normal k is also the proper and correct change per degree of its molecular function.

Attention is called here to the fact that this calculated t_c need not always agree with the observed value of the critical temperature, which would indicate that while some liquids are in corresponding states when equally removed from their critical temperatures, others are so only when equally removed from another, fictitious, one.

IV. Aniline, pyridine, and quinoline from this point of view are shown

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to be perfectly normal in molecular weight, even from the results of capillary rise, although the customary method of calculating k shows the two first to be associated, and the latter dissociated. This confirms the results of drop weight, which being freer from variable error shows the k value for these to be normal, even when calculated in the customary way.

V. It is shown that the application to drop weights of the empirical formula for the calculation of t_c, without a knowledge of the molecular weight, as given by Walden, leads to results which differ but slightly from those calculated by the aid of the normal constant k_B.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 187.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. V. THE DROP WEIGHTS OF FIFTEEN NON-ASSOCIATED LIQUIDS AS FOUND BY USE OF THE NEW FORM OF APPARATUS, AND THE MOLECULAR WEIGHTS CALCULATED FOR THEM.

BY J. LIVINGSTON R. MORGAN AND EDGAR G. THOMSSEN.

Received March 16, 1911.

Introduction.

The object of this paper is to present the results of a testing of the Morgan drop weight apparatus, recently described, for the following purposes:

I. To show that the results of Morgan and Higgins can be duplicated with an apparatus of such simplicity that it can be used as a general laboratory method.

II. To apply the new definition of normal molecular weight of a liquid, recently presented by Morgan, and expressed solely in the equation $w(M/d)^{2/3} = k(t_c - t - 6)$, to further liquids; *not only to those cases where the calculated value of t_c, constant at all temperatures of observation, agrees with the observed critical temperature, but also, and especially, to those where it does not.*

The Standardization of the Tip.

Several months were spent at the beginning of this research on a study of the best form of tip to be used in the new apparatus, where a number of drops, formed successively, are weighed. The beveled tips which, naturally, were first tried, showed apparently that slight differences in the angle of the bevel caused differing results, although several beveled tips were found to be excellent. It was just at this time, however, that it was found possible by the grinder to produce the straight sharp-edged tips already described, so that no further work was done with beveled ones. It must be conceded, therefore, that *in the light of our present knowledge, when all the possible variables affecting a tip are known, no*

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very thorough test has been made of beveled tips, so that it is quite likely that in result they would now be found quite as satisfactory as those with the straight sharp edges. The use of these latter, however, it must be confessed, is more satisfactory for other reasons, for on them any rise of liquid on the edge can be at once recognized; the diameter can be measured more accurately, and any attempted mathematical treatment is simplified, owing to the fact that the only variable of the tip necessary to be considered is its diameter.

The diameter of the straight-edged tip used in this research was approximately 5.63 millimeters, the bore being about 0.2 millimeter. The experimental results obtained with this tip for the six liquids already investigated by Morgan and Higgins, with the more elaborate form of apparatus, are contained in Tables I–VI.

TABLE I.—BENZENE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
18	11.2498	11.2498	10.4758	10.4758	18	30.96
18	11.2498		10.4758			
60.3	11.0865	11.0863	10.4587	10.4587	60.3	25.104
60.3	11.0861		10.4587			

TABLE II.—QUINOLINE.

18	11.7616	11.7615	10.5590	10.5590	18	48.10
18	11.7614		10.5590			
60	11.6091	11.60915	10.5316	10.5318	60.05	43.094
60.1	11.6092		10.5320			

TABLE III.—CARBON TETRACHLORIDE.

18.7	11.2020	11.20185	10.4805	10.4806	18.7	28.85
18.7	11.2017		10.4807			
59.1	11.0679					
59.25	11.0680		10.4792			
59.4	11.0668	11.0673		10.47845	59.34	23.554
59.5	11.0666		10.4777			
59.45	11.0672					

TABLE IV.—CHLOROBENZENE.

18.3	11.3892	11.3893	10.4926	10.4926	18.3	35.868
18.3	11.3894		10.4926			
60.5	11.2365	11.2367	10.4748	10.4748	60.5	30.476
60.5	11.2369		10.4748			

TABLE V.—ANILINE.

22	11.6913	11.69115	10.3167 (empty vessel)	22	45.815
22	11.6910				
60.5	10.5229 (5 drops)		10.3206 (empty vessel and vapor)	60.5	40.475
60.5	10.7255 (10 drops)				

TABLE VI.—PYRIDINE.

18.2	11.5238	11.52375	10.5145	10.5145	18.25	40.37
18.3	11.5237		10.5145			
60.1	11.3456	11.3458	10.4926	10.4924	60.1	34.136
60.1	11.3460		10.4922			

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These results were obtained more than a year ago, before the effect of even the slightest trace of impurity in the liquid was observed (for none but the purest samples were studied by Morgan and Higgins), and before the necessity of washing out the tip and ventilation tubes with ether between determinations of aniline and such liquids was recognized. But although somewhat better results, in the light of our present knowledge, can be obtained for these liquids to-day, these are presented here as the first results obtained with the later form of apparatus. The main object of this test was to show that, using the critical temperatures actually calculated by Morgan and Higgins for these six liquids, from their practically identical value of $k_{\text{temp.}} = \Delta[w(M/d)^{2/3}]/\Delta t$, a k value can be calculated from the results on the later form of apparatus which is also practically identical at all temperatures. For this purpose the k values necessary to give t_c in $w(M/d)^{2/3} = k(t_c - t - 6)$ a value equal in each case to that found for that liquid by Morgan and Higgins have been calculated, and are presented in Table VII. The densities employed here are those calculated by aid of the following formulas, obtained from the values experimentally determined by Morgan and Higgins.

Benzene, $d_t = 0.90022 - 0.001066\ t$.
Quinoline, $d_t = 1.10989 - 0.0008035\ t$.
Chlorobenzene, $d_t = 1.12870 - 0.001092\ t$.
Pyridine, $d_t = 1.00150 - 0.001002\ t$.
Aniline, $d_t = 1.03880 - 0.0008605\ t$.
Carbon tetrachloride, $d_t = 1.62965 - 0.001956\ t$.

TABLE VII.—VALUES OF $w(M/d)^{2/3}$ AND OF k.

Liquid.	M.	t.	w.	d.	$w(M/d)^{2/3}$.	k necessary to give tc of M. and H.		
Benzene....	78	18	30.960	0.88103	614.993	2.3260	2.3257	288.4°
		60.3	25.104	0.83594	516.443	2.3253		
Quinoline...	129	18	48.100	1.0943	1156.415	2.3296	2.3286	520.4°
		60.05	43.094	1.0616	1057.230	2.3269		
Chloroben-zene.....	112.5	18.3	35.868	1.1087	780.308	2.3279	2.3277	359.5°
		60.5	30.476	1.0626	682.003	2.3276		
Pyridine....	79	18.25	40.370	0.9832	751.707	2.3298	2.3297	347.0°
		60.1	34.136	0.9413	654.353	2.3295		
Aniline.....	93	22	45.815	1.0199	928.164	2.3332	2.3320	425.8°
		60.5	40.475	0.9867	838.273	2.3331		
Carbon tetra-chloride...	153.8	18.7	28.850	1.5931	607.140	2.3307	2.3317	285.2°
		59.34	23.554	1.5136	512.895	2.3328		
						Average,	2.3294 ± 0.001 (= 0.05%)	

Here it is quite evident that the tip is too large for the use of carbon tetrachloride, for even the above results, which were only obtained after

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long practice and after many attempts to control the speed of formation of the drop at the moment of fall, were known to lack perfect control, and consequently are certainly slightly too large. In such cases *it is always observed that the error due to lack of control is about the same at all temperatures, when the best control possible on that piece of apparatus is attained; so that the new definition of normal molecular weight is found to hold also under these conditions, although, of course, the constant t_c calculated is larger than that observed with perfect control.* Experiments undertaken since by other observers in this laboratory have shown that when perfect control certainly exists (for example with a tip of about 4.5 mm. in diameter) the t_c calculated for carbon tetrachloride, from its normal (benzene) value of k (*i. e.*, that necessary to give $t_c = 288.5°$, see the previous paper of this series) is reduced by 0.7 per cent. or to 283.2°, which is not only the value to be found from the capillary rise results of Ramsay and Shields, but is also in perfect agreement with the directly observed critical temperature. The agreement of the value in the Table with that of Morgan and Higgins would indicate, then, that the higher value 285.2° as found by them on the 6.2 mm. tip was also high, due to an unsuspected lack of control, even though the long tail of liquid in the fine capillary buret would tend to slow it up considerably. At any rate, with the new form of apparatus, it is quite certain that if carbon tetrachloride is to be included in the liquids studied with any one piece of apparatus, and the drop perfectly controlled, as are those of all the other liquids, the tip must not be larger than about 4.5 mm., upon which all other liquids also give satisfactory results.[1]

The aniline values here are slightly larger than those which are now being found, taking the necessary precautions, as made clear in No. III of this series, and are due either to the fact that the aniline was not freshly distilled just before the experiment, or to the unrecognized presence of very small threads of liquid which were pushed ahead of the drop. This difficulty is now avoided by washing out the bore with ether between determinations, and then preventing any rise of liquid in the tube until the first drop is sucked over. The results for pyridine are also slightly larger than those now being found, which is probably due to a very slight impurity in the sample used.

The above values for chlorobenzene are not those found by the usual procedure, but only when the drops are formed very rapidly and then checked suddenly at the last moment. In this case there is no question of the drop forming too rapidly, and thus giving too high a result, but rather that any evaporation back to the hanging drop from the liquid which has already fallen, such as was observed by Morgan and Higgins,

[1] In a later paper will be given the results of an extended study with various liquids on tips varying from 3 to 8 millimeters.

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is prevented. That this higher result is not due to rapid formation can be shown by first placing in the weighing vessel a small amount of albolene, containing some chlorobenzene, and, after getting its weight, placing it upon the apparatus, and allowing 30 drops to form in the usual way. Each drop as it falls now sinks below the surface of the albolene, and consequently none of the fallen liquid can evaporate back to the hanging drop. Naturally, a blank of 5 drops must also be treated in the same way. This form of procedure leads to the same results as the above, using $t_c = 359.5°$[1] The *usual* procedure here, on the new form of apparatus, in contrast to this leads in all cases to the correct k value only when t_c is taken as 357.5°, and it is a question which is the correct value, the one requiring the use of $t_c = 357.5°$, as obtained by every one using the regular procedure and agreeing with the capillary rise value of Ramsay and Shields; or the 359.5°, which is only obtained under other conditions, and agrees more closely with the observed value of the critical temperature. *It is thought, however, that the 357.5° value is the correct one, as there seems to be no behavior of the liquid which would not be corrected by the 5-drop blank, with the 6th drop hanging long enough to make the elapsed time equal in both cases.*

Even though the results above are not quite as accurate as those which are now being obtained, *and sources of error are undoubtedly found which would correct under proper conditions, with the new form of apparatus, the values of carbon tetrachloride and of chlorobenzene of Morgan and Higgins, it will be seen that they check very satisfactorily those of the latter on the more elaborate apparatus (and this on a smaller tip, which has a straight sharp edge, instead of being beveled) for in both cases the mean error in the k value is about the same.*

This, of course, is not the best way to standardize a tip, and is used here only to show that the results of Morgan and Higgins can be duplicated on the simpler form of apparatus. The best method of testing the k value of a tip as found from benzene by assuming its t_c to have the value 288.5°, the observed critical temperature, is to calculate the value of k necessary to give t_c the values found by Morgan and Higgins from their normal (benzene) value of k, see previous paper of this series. These values, as corrected, are 357.5° for chlorobenzene, 425.7° for aniline, 283.2° (a tip of 4.5 mm.) for carbon tetrachloride, 346.6° for pyridine, and 521.3° for quinoline. These values of k will not disagree, with careful work and pure liquids, by more than one-tenth of one per cent., if by as much.

It is evident here that drop weights from this tip are related, at the same temperature, to those found on that of Morgan and Higgins, as the k

[1] Miss C. M. Sillcox is now investigating this and another liquid in this way.

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value above for benzene ($t_c = 288.5°$) is to the correspondingly found value of k for their tip, *i. e.*,

$$w_{M\,\&\,T} : w_{M\,\&\,H} :: 2.3257 : 2.5702;$$

and that the surface tension in dynes per centimeter can be calculated from the drop weights in milligrams by aid of the proportion

$$\gamma : w_{M\,\&\,T} :: k : 2.3257,$$

where k would be the value for benzene found by the observer whose work is to be compared with drop weight; or the average value of k found by all those who have worked with the capillary rise method on benzene.

New Liquids.

The new liquids selected to show the application of the method, and of the new definition of normal molecular weight in the liquid state, are the following; ether, ethyl *n*-butyrate, chloroform, phenetole, anisole, benzonitrile, ethylene dibromide, carbon disulfide, and a mixture of equal weights of benzene and carbon tetrachloride.

The experimental results for these are given in Tables VIII to XVI, inclusive.

TABLE VIII.—ETHER.

t.	Wt. vessel + 30 drops.	Av.	Wt. vessel + 10 drops.	Av	Av. *t.*	Wt. 1 drop. Mg.
25.6	8.7111		8.3681			
26.0	8.7089	8.70933	8.3674	8.36775	25.9	17.079
26.1	8.7080					

TABLE IX.—ETHYL *n*-BUTYRATE.

	+ 25 drops.		+ 5 drops.			
26.2	11.0712	11.0707	10.5746	10.5749	26.4	24.74
26.6	11.0702		10.5752			
59.0	10.9722					
59.3	10.9708	10.9714	10.5458	10.5456	59.2	21.29
59.3	10.9712		10.5454			

TABLE X.—CHLOROFORM, b. p. = 61.2°.

22.4	10.7930	10.7926	10.2139	10.2135	22.45	28.955
22.5	10.7922		10.2131			
60.0	11.4155					
60.1	11.4233		10.9512			
60.3	11.4230	11.4221	10.9525	10.9520	60.18	23.595
60.3	11.4266		10.9523			

TABLE XI.—PHENETOLE.

	+ 30 drops.					
22.9	11.7286					
23.1	11.7288	11.7289	10.8665	10.86675	23	34.486
23.0	11.7293		10.8670			
60.0	11.6042					
60.3	11.6031	11.6031	10.8462	10.84675	60.2	30.254
60.3	11.6023		10.8473			

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TABLE XII.—BENZONITRILE.

t.	Wt. vessel + 30 drops.	Av.	Vessel + 5 drops.	Av.	Av. t.	Wt. 1 drop. Mg.
21.8	11.9303					
21.6	11.9301	11.9303	10.8987	10.8987	21.63	41.264
21.5	11.9304					
60.1	11.7868	11.78705	10.8795	10.8794	60.1	36.306
60.1	11.7873		10.8793			

TABLE XIII.—ANISOLE.

22.5	11.8027	11.8029	10.8797	10.87995	22.45	36.918
22.4	11.8031		10.8802			
60.0	11.6663	11.6661	10.8575	10.8574	60.0	32.348
60.0	11.6659		10.8573			

TABLE XIV.—ETHYLENE DIBROMIDE.

24.4	12.0607	12.0606	11.0272	11.0272	24.3	41.336
24.2	12.0605					
60.5	11.9143	11.9140	11.0084	11.0084	60.5	36.224
60.5	11.9137		11.0084			

TABLE XV.—CARBON DISULFIDE.

24.5	11.8167	11.81705	10.9819	10.98175	24.4	33.412
24.3	11.8174		10.9816			
3.9	11.9283	11.9290	11.0013	10.00155	3.8°	37.098
3.7	11.9297		11.0018			

TABLE XVI.—BENZENE AND CARBON TETRACHLORIDE; 1 : 1 BY WEIGHT.

23.6	11.6925	11.6926	10.9677	10.9676	23.6	29.00
23.6	11.6927		10.9675			

To show that the new definition of normal molecular weight (see No. IV of the series) may be applied to the above liquids, *i. e.*, to prove that using the normal (benzene) value of k, as found from the relationship $w(M/d)^{2/3} = k_B(288.5—t—6)$, in $w(M/d)^{2/3} = k_B(t_c—t—6)$, will give a constant value, within the limits of error, of the calculated t_c for each new liquid, independent of the temperature of observation t, the values of the functions $w(M/d)^{2/3}$, together with the calculated value of t_c at each temperature, are given in Tables XVII to XXV. At the same time the corresponding values of the function, expressed as a surface tension in dynes, as found from capillary rise, and the calculated values of t_c as found from the benzene value, k_B, of the same observer, are given, so far as they are to be found in the literature.

This method of comparing drop weight with surface tension (and the results of the latter among themselves) is used here in preference to the one involving the direct transformation of w into γ, because of the fact that the temperatures of observation are not the same, and it is desired to avoid any interpolation so long as the direct experimental results can be employed. In essence it will be seen that this comparison, by finding

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the calculated t_c from the work of each observer, *i. e.*, from the equations

$$\gamma(M/d_1)^{2/3} = k_B(t_c—t_1—6)$$

and

$$w(M/d_2)^{2/3} = K_B(t_c—t_2—6),$$

where M is the same in all cases for the same liquid, γ/k_B is equal to w/K_B, and d_1 and d_2 are dependent in the same way upon the temperature t, is the same as transforming the drop weight w in milligrams, into surface tension in dynes, γ, (by multiplying it by the ratio k_B/K_B) and then by the use of the same k_B to show that the $\gamma(M/d)^{2/3}$ is the same function of the temperature, whether calculated from drop weight or capillary rise, and consequently leads to the same calculated t_c. *In other words, when the same t_c is thus found from the results of drop weight, and from those of capillary rise, it means that*

$$\gamma : w : k_B : : K_B,$$

at the same temperature, is the correct relationship for that liquid.

Perhaps the greatest advantage offered by this method of comparison is the saving in the calculation necessary, for if the γ values were calculated from the drop weight, they would all differ slightly, according as the k_B values of the various observers in question differ; and as many values of γ would have to be calculated as there are individual observers, whose results are to be contrasted, before calculating, for the equalization of the temperature, a t_c value from each, with its own proper k_B value. By the method chosen, however, all this is avoided, by simply finding from the work of each observer *the value of t_c resulting from his function value and temperature, by use of his normal (benzene) k value, and then comparing them.*

One thing must be remembered here before drawing any conclusion as to the results of surface tension found by the transformation of w into γ by multiplying it by k_B/K_B, *viz.:* the *value of surface tension in dynes, as calculated from the drop weight is a directly determined weight, multiplied by a ratio, which can be found once for all with practically any desired degree of accuracy. Surface tension when calculated from capillary rise, on the other hand, is a value found by multiplying one-half the radius (assumed to be the same throughout) of a very fine capillary bore, by the density of the liquid, less that of the vapor, by a height of ascension in that tube, which is burdened with a correction for the volume of the meniscus, which may amount to as much as from 6 to 9 per cent.* Further than this, the function value $^1/_2\, h\, r\, (d_l—d_v)(M/d)^{2/3}$ is affected to double the percentage extent that $w(M/d)^{2/3}$ is (neglecting the value of d_v), by a known error in d, as can be shown by a differentiation of the two functions and then dividing them by the original values.

As is also evident here, from the drop weight it is possible to find a number

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which is proportional to the so-called capillary constant at that temperature, provided the density is also known at that point. This can be shown as follows: Since

$$w_t \propto \gamma_t$$

and

$$\gamma_t = {}^1/_2\, h_t\, r\, (d_e - d_v),$$

while for the capillary constant a^2 we have the relationship

$$a_t^2 = h_t r,$$

it follows that

$$w_t/d_t \propto \frac{{}^1/_2\, h_t\, r\, d_t}{d_e - d_v},$$

and

$$v_t = w_t/d_t = \text{constant} \times a_t^2; \text{ or } v_t \propto a_t^2.$$

The capillary constant of any liquid varies directly as the volume of the drop, falling from any one tip, at that temperature.

TABLE XVII.—ETHER, M = 74.08; t_c obs. = 194.5°.

t.	w.	d.	$w(M/d)^{2/3}$.	t_c from $k_\beta = 2.3257$.
25.9	17.079	0.7071	379.56	195.1°
	Ramsay and Shields,[1] k_B = 2.1012.			
20	..	..	363.7	199.1
40	..	..	317.4	197.1
70	..	..	251.0	195.5
80	..	..	229.5	195.2
80	..	..	229.5	195.2
90	..	..	208.1	195.0

TABLE XVIII.—CHLOROFORM, M = 119.33, t_c obs. = 260° and 258.8°.

22.45	28.955	1.4840	539.43	260.6
60.18	23.505	1.4107	451.59	260.4[2]

TABLE XIX.—ETHYL *n*-BUTYRATE, M = 116.096; t_c obs. = 292.8° and 304.3°.

26.4	24.79	0.87207	646.33	310.3
59.2	21.29	0.83710	570.41	310.4

TABLE XX.—PHENETOLE, M = 122.08; t_c obs. = 374°.

23.0	34.486	0.9638	869.79	403.0
60.2	30.254	0.9278	782.67	402.7
	Renard and Guye,[3] k_B = 2.1108.			
10.5	33.19	0.976	830.11	406.0
44.0	29.15	0.944	745.42	403.2
52.1	28.31	0.936	728.09	403.0
63.9	27.07	0.925	701.71	401.9
71.7	26.21	0.917	683.07	401.5

[1] *Z. physik. Chem.*, 12, 431 (1893).
[2] Boiling point of chloroform is but 1° above this temperature.
[3] *J. Chim. Phys.*, 5, 81 (1907).

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t.	w.	d.	$w(M/d)^{2/3}$.	t_c.
88.9	24.39	0.901	643.42	399.7
99.6	23.20	0.890	617.06	397.9
117.8	21.45	0.873	577.89	397.6
133.1	19.87	0.857	542.05	395.9
150.6	18.28	0.840	505.31	396.0
164.9	16.79	0.825	469.73	393.4
	Guye and Baud,[1] k_B = 2.1012.			
19.2	32.60	0.9672	819.91	415.7
63.6	27.25	0.9249	706.1	405.6
108.7	22.70	0.8818	607.3	403.7
152.4	18.22	0.8380	504.2	398.4
	TABLE XXI.—ANISOLE, M = 108.06; t_c obs. = 368.5°.			
22.45	36.918	0.9900	843.19	391.0
60.0	32.348	0.9563	756.07	391.1
	Renard and Guye, k_B = 2.1108.			
11.1	35.02	1.000	794.5	393.5
33.5	32.51	0.980	747.6	393.7
54.0	30.00	0.962	698.4	390.9
63.1	28.86	0.953	676.1	389.4
76.1	27.47	0.940	649.5	389.8
88.0	26.12	0.929	622.5	388.9
98.6	24.97	0.918	599.7	388.7
109.0	23.74	0.908	574.4	387.1
119.0	22.64	0.897	552.2	386.6
135.9	20.86	0.880	515.4	386.1
147.9	19.59	0.868	488.4	385.3
	Guye and Baud, k_B = 2.1012.			
9.0	35.48	1.0022	803.5	397.4
54.6	30.36	0.9610	695.9	391.8
98.8	24.80	0.9178	595.5	388.2
152.9	19.28	0.8622	482.6	388.6
	TABLE XXII.—BENZONITRILE, M = 103.05; t_c obs. = 426.2°.			
21.63	41.264	1.0020	905.8	417.1
60.10	36.306	0.9674	815.8	416.9
	Renard and Guye, k_B = 2.1108.			
12.3	38.44	1.012	838.2	415.4
21.0	37.43	1.004	820.5	415.7
30.5	36.41	0.995	803.0	416.9
46.8	34.54	0.980	769.5	417.4
59.1	33.24	0.969	746.1	418.6
67.8	32.30	0.963	728.0	418.7
86.8	30.19	0.944	689.6	419.5
99.8	28.83	0.932	664.2	420.4

[1] *Arch. sci. phys. nat.*, 4th series, 11, 449–471, and 537–556 (1901). These authors used Ramsay and Shields' values of γ for benzene to find the radius of their capillary, hence k_B of Ramsay and Shields is employed above.

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t.	w.	d.	$w(M/d)^{2/3}$.	t_c.
108.9	27.85	0.924	645.3	420.6
131.3	25.49	0.904	599.3	421.2
150.1	23.66	0.887	563.3	423.0
167.0	22.03	0.872	530.5	424.3
184.1	20.42	0.856	479.9	426.0
	Guye and Baud, $k_B = 2.1012$.			
8.0	39.61	1.1016	861.4	424.0
54.9	33.82	0.9726	757.0	421.2
99.1	29.30	0.9388	673.9	425.8
152.4	23.53	0.8848	561.0	425.4
	Ramsay and Shields, $k_B = 2.1012$.			
18.1	36.22	1.0070	792.7	401.4
46.3	32.88	0.9806	731.8	400.6
78.3	29.29	0.9526	664.8	400.7

TABLE XXIII.—ETHYLENE DIBROMIDE,[1] M = 187.87; t_c obs. = 309.8°.

24.3	41.336	2.1623	810.88	379.0
60.5	36.224	2.0886	727.22	379.2
	Ramsay and Aston, $k_B = 2.1211$.			
12.2	38.91	2.1873	757.7	375.4
44.9	34.57	2.1189	687.7	375.1
77.2	30.37	2.0502	617.6	374.4
131.3	23.74	1.9315	502.2	374.1

TABLE XXIV.—CARBON DISULFIDE; M = 76.14; t_c obs. from 271.8° to 279.6°.

3.8	37.098	1.2865	563.4	252.1
24.4	33.412	1.2556	515.7	252.1
	Ramsay and Shields, $k_B = 2.1012$.			
19.4	33.58	1.264	515.4	270.2
46.1	29.41	1.223	461.4	271.7
	Ramsay and Aston,[2] $k_B = 2.1211$.			
9.7	32.73	1.2773	499.2	251.1
46.0	27.68	1.2224	434.8	257.0
61.0	25.35	1.1980	403.6	257.4

TABLE XXV.—BENZENE AND CARBON TETRACHLORIDE, 1 : 1 BY WEIGHT.[3]

Av. M = 115.9, Av. t_c = 287.1° $\left(i.e., \frac{288.5 + 285.8}{2}\right)$.

23.6	29.00	1.2293	600.74	287.9
	Ramsay and Aston, $k_B = 2.1211$, t_c calc. = 286.5.[4]			
16°	27.70	1.2597	561.9	286.9
46.2	23.50	1.2095	492.0	284.2
78.2	19.71	1.1596	424.5	284.3

[1] This liquid gives a drop volume of the same order as carbon tetrachloride, so this value may be too high, but at any rate its constancy by both methods shows normal molecular weight.

[2] The authors state that it was impossible to duplicate the higher results of Ramsay and Shields.

[3] No special precautions were taken in making this mixture.

[4] Ramsay and Aston find a mean of 284.6° for t_c for carbon tetrachloride from this k_B (see No. IV of this series). The value above is $\frac{288.5 + 284.6}{2}$.

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The calculation of t_c by the modified relationship of Walden (see the previous paper) t_c = constant $\frac{\alpha' + \alpha''}{\alpha'\alpha''}$ (where α' and α'' are found from the relations $\gamma_t = \gamma_o(1-\alpha' t)$ and $a_t^2 = a_o^2(1-\alpha'' t)$) using the values found from the drop weight and drop volume relations

$$w_t = w_o\,(1-\alpha' t),$$
$$v_t = v_o\,(1-\alpha'' t),$$

which, as has already been shown, should give the same α' and α'' values as the others, for they are only a percentage change, are given for those liquids studied at two temperatures, in Table XXVI. These values, naturally, are burdened with the same kind of a multiplied error as k is, when it is calculated from the equation $k = \Delta[w(\mathrm{M}/d)^{2/3}]/\Delta t$. Thus if the high temperature value is slightly high, while that at the low is slightly low, the temperature coefficient $\Delta w/\Delta t$ from which α' is calculated will be too small, etc. The object here is to show that even with this error, and without the use of a molecular weight, sensibly the same value (within the limits of error of this form of calculation) of t_c is found by this method as by that involving k_B found from

$$w(\mathrm{M}/d)^{2/3} = k_B(288.5^\circ - t - 6)$$

for benzene.

TABLE XXVI. t_c = Constant $\frac{\alpha' + \alpha''}{\alpha'\alpha''}$.[1]

Liquid.	α'.	α''.	t_c.	t_c from k_B.
Quinoline	0.0023695	0.0017613	518.6°	...
Pyridine	0.003457	0.0026552	348.9	...
Carbon tetrachloride	0.0041652	0.0032519	287.0	...
Chlorobenzene	0.0033443	0.0025621	361.2	...
Aniline	0.0028384	0.0021484	428.5	...
Ethyl *n*-butyrate	0.0038652	0.0029601	312.6	310.3
Chloroform	0.0044832	0.0035579	264.2	260.5
Phenetole	0.0030662	0.0022613	402.7	402.9
Anisole	0.0030695	0.0023442	394.2	391.0
Benzonitrile	0.0029256	0.0021957	415.9	417.0
Ethylene dibromide	0.0031544	0.0024119	383.4	379.1
Carbon disulfide	0.0047364	0.0036947	252.5	252.1

Discussion of Results.

It is quite evident from the above Tables that the new definition of normal molecular weight is perfectly fulfilled, according to the drop weight method, for all the liquids. *Our only conclusion, then, is that the above liquids, since they give a value of t_c from the normal (benzene) value of k_B in the equation $w(\mathrm{M}/d)^{2/3} = k_B\,(t_c - t - 6)$, which is constant, independent of the temperature of observation, are perfectly normal in behavior, and consequently are non-associated.*

[1] The constant is found from benzene for which $\alpha' = 0.0041385$, $\alpha'' = 0.0032373$, and $t_c = 288.5^\circ$; and has the value 0.52404.

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It must not be thought that the experimental results given in the Tables were the only ones from which a drop weight of the same value could be calculated. Immediately after each 30-drop determination, a 5-drop blank was made, at nearly the same temperature as possible, so that a series of drop weights at perhaps slightly varying (within 0.2° to 0.5°) temperatures were thus obtained. Within a very slight error these all led to the same value of t_c. The weights given in the tables, beside showing the maximum deviation observed, also lead in all cases to a value giving the same t_c that the average of all, at an average temperature, would give. Granting perfectly constant temperature, there is no reason why the extreme deviation in total weight of the vessel and drops should amount to more than 2 or 3 tenths of a milligram.

It will be observed that only in the cases of ether and chloroform do the calculated t_c values agree with the observed critical temperatures, although the agreement for these two liquids is remarkable. In the other cases, since the t_c is constant (within very small limits), independent of the temperature of observation, it is proof that the normal (benzene) value of k_β is also the correct and proper temperature coefficient of $w(M/d)^{2/3}$ for these liquids; *hence as to molecular weight they are to be considered just as normal and just as much non-associated as benzene itself, although the fictitious critical temperature* t_c, *i. e., the point at 6° below which* $w(M/d)^{2/3}$, *by the equation, becomes zero, does not coincide with the observed critical temperature.* One question arises here which probably must remain open for some time, and which may be stated as follows: Is the observed critical temperature ever influenced by a decomposition of the liquid, due to heat or the presence of mercury, before it reaches that point? It may be said here that ethylene dibromide when heated to a point below the critical in a closed tube, in the presence of mercury, certainly does decompose, as is evidenced by the pressure on opening the tube after cooling. When a gas is thus formed, naturally the observed critical temperature will be lower than it should be, owing to the presence of the gas, with its necessarily low critical temperature; in other words, it will be the mean critical temperature of the mixture that is measured, rather than that of the undecomposed liquid. Such a process might account for the higher fictitious critical temperature t_c calculated for this liquid both by drop weight and by capillary rise. This, of course, would only be true for a limited number of liquids, and would not account in general for the discrepancy existing between the fictitious and the observed critical temperatures.

Although ether was studied here at but one temperature, results by another observer on this tip, at both 0° and 27.8°, lead to the same value of the calculated t_c. Why Ramsay and Shields' value of t_c should have a downward trend is unknown. The drop weight leads to the same t_c at

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0° as at other temperatures, while capillary rise gives this value only between 70° and 90°. *We must conclude, then, that either drop weight is not proportional to surface tension at all, in which case we must assume the unlikely thing that the agreement of the value found by the former, at all temperatures, with the value of the latter between 70° and 90° is accidental; or, and it seems that this is the only logical conclusion, they are strictly proportional, but there is a large variable error in the results of capillary rise at times.* This latter seems still more likely when it is recalled that the height of ascension of ether in a capillary tube is very small at all temperatures.

For chloroform and ethyl *n*-butyrate, no surface tensions could be found in the literature, so that a direct comparison is impossible, but the excellent agreement of t_c with the observed value, in the former case, and the not excessive variation in the latter, especially as both show a value of t_c which is independent of the temperature of observation, makes a comparison perhaps unnecessary. The higher chloroform temperature here is out about 1° below the boiling point.

In the case of phenetole, Renard and Guye find a decided trend downward with increasing temperature, but the results of Guye and Baud, although showing a trend, lead to higher values of t_c throughout; so that the former at 40° to 52.1°, and the latter at 108.7° agree with the drop weight at both its temperatures. Assuming the variation in the values of capillary rise to be due to variable error, and then getting the mean t_c of both Renard and Guye (397.7°) and Guye and Baud (405.8°) we find 402.7° as compared to the individual values 402.7° and 403° found from drop weight.

For anisole, we find also a trend downward in the values of t_c of both Renard and Guye and Guye and Baud, the values of Guye and Baud, just as with phenetole, being the larger throughout. Again assuming this to be due to variable error, and getting the mean, we find for the former 389° and for the latter 391.5°, which leads to 390.1°, as compared to the constant value 391° from drop weight. For benzonitrile the results from capillary rise are most confusing. Here the trend of the results of Renard and Guye is upward, agreeing with drop weight at 21.6 and 60°. Guye and Baud, on the other hand, find values varying around 424° at all their temperatures, while Ramsay and Shields find about 401° for their three temperatures. Certainly drop weight here agrees with every value as well as any of the capillary rise values agree with any other, but no comparison can be made because the non-agreement of the results from capillary rise makes it impossible to find any one number to compare the drop weight with.

In the case of ethylene dibromide, the drop weight result may well be a trifle high (as is the case with the similar liquid carbon tetrachloride),

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for this drop has a very small volume, and lack of control, even though slight, would cause an error, owing to the very great density. At any rate, here the calculated values of t_c are constant, as they also are, although of a slightly different value, when calculated from the capillary rise. The Ramsay and Shields result for carbon disulfide could not be confirmed by Ramsay and Aston, who spent considerable time in the attempt, especially at low temperatures. The specimen used for the drop weight, though called pure, and redistilled several times, still had an unpleasant odor. Later, a report will be made upon the work on a specimen so pure that it has its supposedly characteristic pleasant ethereal odor. For the mixture of benzene and carbon tetrachloride a t_c is found which differs but slightly from the mean of those found for the components. The value of Ramsay and Aston, at the lower temperature, also agrees well with the mean of their observed values, but the others do not seem to be very constant, which may be due to changes in the mixture on heating.

By the above treatment drop weight and surface tension from capillary rise are shown to be proportional, at least in those cases where it is possible to find from the work of observers with the latter method any one approximate value upon which they can agree, and with which the drop weight result can be compared. *One thing at least is clear with respect to capillary rise, viz.: that a variable error exists. Allowing for this error, it will be seen that surface tension from capillary rise also shows by the new definition of normal molecular weight that the above liquids are normal and non-associated. Further, wherever the results of capillary rise can be confirmed by other observers, it will be noticed that the fictitious critical temperatures t_c are the same when found from capillary rise, as when found from drop weight.*

In the next paper of this series will be considered the results of 20 other non-associated liquids, together with the corresponding values found by capillary rise.

Summary.

The results of this investigation may be summarized as follows:

I. From drop weight results it is shown that, using the new criterion of normal molecular weight, *viz.:* the finding of a value of t_c, using the normal (benzene) value of k_B, in the equation $w(M/d)^{2/3} = k_B (t_c - t - 6)$, which is constant, independent of the temperatrue of observation, is fulfilled for ether, ethyl *n*-butyrate, anisole, phenetole, ethylene dibromide, chloroform, benzonitrile and carbon disulfide, which consequently are non-associated. This same conclusion can be reached from the results of capillary rise (when they are given), provided we assume in that method the presence of a not excessive variable error.

II. Only in the cases of ether and chloroform do the values of t_c as calculated agree closely with the observed critical temperatures, but the

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fictitious values of the critical temperature found for the others agree with those that are calculated from the capillary rise.

III. The values of t_c both true and fictitious, found by aid of the modified Walden method, applied to drop weight, without the use of the molecular weight, agree as closely as could be expected, remembering the possibilities of error inherent in the method.

IV. It is shown that the calculated t_c for a mixture of benzene and carbon tetrachloride, 1 : 1 by weight, is practically the mean of the values found for these two liquids alone.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 188.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. VI. THE DROP WEIGHTS OF TWENTY NEW NON-ASSOCIATED LIQUIDS, AND THE MOLECULAR WEIGHTS CALCULATED FOR THEM.

BY J. LIVINGSTON R. MORGAN AND G. K. DAGHLIAN.

Received March 27, 1911.

The object of this paper is to present the results of a further testing of the Morgan drop weight apparatus, similar to that carried out by Morgan and Thomssen, for the purpose of testing the new definition of normal molecular weight, and comparing the results with those found from the capillary rise, wherever that is possible; studying those liquids which lead to a calculated value of t_c in $w(M/d)^{2/3} = k\ (t_c - t - 6)$, which agrees with the observed critical temperature, as well as those which do not.

The tip used in this research was one with a sharp, straight edge, having a diameter of about 5.7 mm., with a bore of 0.2 mm. It was at once recognized here that it would be impossible on this tip to use any liquid of such a great density and small surface tension as carbon tetrachloride, as it would produce a drop too small in volume to be controlled, so that liquid was not studied. All the other liquids gave drops of such a volume that their speed of formation at the moment of fall could be perfectly controlled.

The experimental results for the standardization of this tip, using benzene, aniline, pyridine, and quinoline, are given in Table I to IV inclusive:

TABLE I.—BENZENE.

t.	Wt. vessel + 15 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. t.	Wt. 1 drop. Mg.
36.05	10.0871					
36.05	10.0868	10.0869	10.7954	10.7955	36.15	29.14
36.35	10.0868		10.7956			
59.58	10.0472					
59.53	10.0474	10.0471	10.7883	10.7883	59.54	25.88
59.53	10.0467		10.7883			

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TABLE II.—ANILINE.

t.	Wt. vessel + 15 drops.	Av.	Wt vessel + 5 drops.	Av.	Av t.	Wt. 1 drop. Mg.
34.3	10.0954					
34.2	10.0960	10.0956	10.6440 (empty vessel and vapor)		34.3	45.16
34.35	10.0960					
34.3	10.0950					

TABLE III.—PYRIDINE.

23.03	11.2548					
22.75	11.2550	11.2549	10.8484	10.8483	22.93	40.66
23.13	11.2544		10.8482			
22.83	11.2553					
	Vessel + 25 drops.					
58.33	10.6389		10.9346			
58.43	10.6384	10.6386	10.9340	10.9343	58.4	35.215
58.40	10.6385					

TABLE IV.—QUINOLINE.

22.38	10.4846	10.4846	9.7525 (empty)		22.33	48.807
22.28	10.4846					

These results were obtained a year ago, and consequently, as were those given in the previous paper, are not as accurate as those which can be obtained now. The k values for these liquids from the above results, using the t_c values actually calculated by Morgan and Higgins from the ratio $k_{temp.} = \Delta[w(M/d)^{2/3}]/\Delta t$, are given in Table V, and will serve to show that the values of k necessary are practically constant. The densities used here are calculated from the formulas already given by Morgan and Thomssen.

TABLE V.—VALUES OF $w(M/d)^{2/3}$ AND OF k.

Liquid.	M.	t.	d.	w.	$w(M/d)^{2/3}$.	k necessary to give t_c of M & H.		
Benzene.....	78	36.15°	0.8617	29.14	587.47	2.3857	2.3866	288.4°
		59.54	0.8368	25.88	532.06	2.3874		
Aniline.....	93	34.3°	1.0093	45.16	921.20	2.3898		425.8
Pyridine.....	79	22.93	0.9785	40.66	759.31	2.3872		347.0
		58.39	0.9430	35.215	674.23	6.3858		
Quinoline.....	129	22.33	1.09195	48.807	1175.17	2.3882		520.4
						2.3874		

Naturally, to transform any result on this tip into one, at the same temperature, on any other tip, we have only to use the proportion

$$w_{M\ \&\ D} : w_x :: 2.3866 : k_x,$$

where k_x is the benzene value of k of the other, calculated from $w(M/d)^{2/3} = k(288.5 - t - 6)$; and to obtain the surface tension in dynes per centimeter, at the same temperature, we have only to use the relation

$$w_{M\ \&\ D} : \gamma :: 2.3866 : k_\gamma$$

where k'_γ is the k value found for benzene as above by the observer whose

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results are to be compared; or is the average value found by all observers who have worked with benzene. While, since the volume of a drop is proportional to the capillary constant, we can calculate the capillary constant a^2 by first finding at the same temperature for benzene the ratio $a^2/w/d$, and then by multiplying any drop volume (*i. e.*, drop weight divided by density) by it, get the capillary constant at that temperature, of the liquid.

Further, it is to be remembered here that surface tensions as calculated from capillary rise can be compared indirectly with the drop weight at another temperature by finding with the proper k_B the value of the calculated t_c for each. An agreement in the values of t_c here indicates, since the M is the same, and d is the same function of the temperature, in each case, that $K : k :: w : \gamma$.

New Liquids.

The experimental results of the 20 new non-associated liquids studied are given in Tables VI to XXV. These results are not as accurate as those which can be obtained, for in many cases only 15 drops were weighed in place of the usual 30, which, with the 5-drop blank, causes an error of 0.1 mg. to become 0.01 in the weight of the single drop. Further, the variation in temperature involves a small error, for it is impossible, when the temperature is changing, to find how much the change in the liquid lags behind that in the thermometer. Notwithstanding these disadvantages, which have been excluded in the papers which are to follow this, it will be observed that the results are very satisfactory. Just as in the last paper, it is to be remembered here also that the results given in the tables throughout are not the only ones which were found, but are representative of a number of results, and are given because the number of drops taken was the same and the temperatures practically identical. In those cases where but one result at each temperature is presented, others were always at hand at a slightly different temperature which checked the value of t_c resulting within less than one-tenth of one per cent.

TABLE VI.—BROMOBENZENE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel. + 5 drops.	Av.	Av. t.	Wt. 1 drop. Mg.
37.9	11.5863					
38.4	11.5870	11.5867	10.8345			
38.55	11.5868		10.8352	10.83485	38.3	37.593
59.63	11.5210		10.8252			
59.70	11.5207	11.52085	10.8247	10.82495	59.67	34.795

TABLE VII.—BROMINE.

	+ 15 drops.					
0	11.4380					
0	11.4376	10.43803	10.9141			
0	11.4385		10.9146	10.91435	0°	52.368

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TABLE VIII.—CARBON DISULFIDE.

t.	Wt. vessel + 15 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. *t.*	Wt. 1 drop. Mg.
20.15	11.1733		10.8190			
20.35	11.1718	11.17337	10.8190	10.8190	20.13	35.437
19.90	11.1750					

TABLE IX.—CYMENE.

18.95	11.0995		10.7963			
18.75	11.1015	11.1009	10.7968	10.79677	18.7	30.413
18.35	11.1018		10.7972			
59.45	11.0406	11.0407	10.7774	....	59.45	26.33
59.45	11.0408					

TABLE X.—DIPHENYLMETHANE.

59.05	11.2108					
59.0	11.2113	11.2110	10.6440 (empty and vapor)		59.0	37.80
58.9	11.2109					

TABLE XI.—ETHYLBENZENE.

20.9	11.1154	11.11545	10.8022	....	21	31.325
21.1	11.1155					
59.4	11.0528	11.05235	10.7846	....	59.5	26.775
59.6	11.0519					

TABLE XII.—DIMETHYLANILINE.

21.45	11.2381	11.2380	10.8419	10.84185	21.5	39.615
21.55	11.2379		10.8418			
59.50	11.1684					
59.65	11.1673	11.1682	10.8192	....	59.5	34.90
59.45	11.1689					

TABLE XIII.—ETHYLANILINE.

35.8	11.2152		10.8355			
35.8	11.2150	11.2152	10.8355	10.8354	35.8	37.98
35.7	11.2154		10.8352			
58.7	11.1760	11.1760	10.8224	10.8225	58.7	35.35
58.7	11.1760		10.8226			

TABLE XIV.—ETHYLENE CHLORIDE.

34.2	11.1483		10.8166			
34.1	11.1484	11.14843	10.8167	10.81665	34.1	33.178
34.1	11.1486					
	+ 26 drops.		+ 6 drops.			
60.0	11.4258	..	10.8404	....	60.0	29.270

TABLE XV.—ETHYLIDENE CHLORIDE.

	+ 15 drops.		+ 5 drops.			
34.1	10.0427		10.7822			
34.1	10.0422	10.04265	10.7822	10.7822	34.1	26.043
34.0	10.0430					
	+ 25 drops.		+ 10 drops.			
56.9	10.2097	..	10.8683	....	56.9	22.76

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TABLE XVI.—TOLUENE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. *t.*	Wt. 1 drop. Mg.
36.05	11.0809	11.08085	10.7916	10.7916	36.05	28.925
36.05	11.0808		10.7916			
59.1	11.0425	11.0423	10.7819	10.78155	59.2	26.075
59.3	11.0421		10.7812			

TABLE XVII.—PHOSPHORUS TRICHLORIDE.

	+ 30 drops.					
35.6	11.5517		10.9567			
35.6	11.5515	11.5514	10.9569	10.9568	35.6	29.73
35.6	11.5510					

TABLE XVIII.—*p*-XYLENE.

	+ 25 drops.		+ 5 drops.			
37.9	11.3678	..	10.7921	....	37.9	28.785
59.2	11.3079	10.3081	10.7820	10.78195	59.2	26.308
59.2	11.3083		10.7819			

TABLE XIX.—*o*-XYLENE.

	+ 15 drops.					
23.9	10.2345	10.23455	9.9144	....	23.85	32.015
23.8	10.2346					
23.7	10.2358	..	9.9153	....	23.7	32.05
59.3	10.1756	10.1753	9.8965	....	59.4	27.88
59.5	10.1750					

TABLE XX.—*m*-XYLENE.

24.9	10.2095	..	9.9057	....	24.9	30.38
58.9	10.1529	..	9.8888	....	58.9	26.41

TABLE XXI.—METHYLANILINE.

	+ 25 drops.					
24.6	10.8230	10.8231	9.9660	9.9659	24.6	42.86
24.6	10.8232		9.9658			
59.7	11.2219	11.2218	10.8378	10.8380	59.7	38.38
59.7	11.2217		10.8382			

TABLE XXII.—MESITYLENE.

	+ 15 drops.					
23.5	10.0844	10.0844	10.7812	10.7812	23.5	30.32
23.5	10.0844		10.7812			
57.1	10.0452	10.0446	10.7787	10.7786	57.3	26.60
57.4	10.0440		10.7785			

TABLE XXIII.—ISOBUTYL ACETATE.

	+ 25 drops.					
24	10.5146	10.5152	10.0082	....	23.8	25.35
23.6	10.5158					
59.2	10.2991	..	9.8680	....	59.2	21.555
59.3	10.4075 (another vessel)		9.9766	....	59.3	21.545

TABLE XXIV.—IODOBENZENE.

23.5	11.9297	..	10.1876	....	23.5	43.55
	+ 30 drops.		+ 10 drops.			
59.6	10.9270	..	10.1441	....	59.6	39.08

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TABLE XXV.—FLUOROBENZENE.

	+ 20 drops.	Vessel and vapor.				
9.3	12.8962					
9.3	12.8965	12.89623	12.2747	....	9.3	31.077
9.3	12.8960					
	+ 25 drops.					
34.5	12.9630		12.4122			
34.5	12.9631	12.96317	12.4126	12.41243	34.5	27.537
34.5	12.9634		12.4125			

In Tables XXVI to XLV, inclusive, are given the values of the function $w(M/d)^{2/3}$ and the calculated t_c resulting from the equation $w(M/d)^{2/3} = k_B(t_c - t - 6)$, using the mean value of the k for benzene, *viz.*, 2.3866. At the same time, wherever it is possible, the surface tension results, as found from capillary rise, together with the calculated value of t_c, from the proper value of k_B, are also given, in order that an indirect comparison may be made of the results of surface tension from drop weight and from capillary rise.

TABLE XXVI.—BROMOBENZENE; M = 156.96; $d_t = 1.5203 - 0.001282t$; t obs. = 397°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
38.3	1.4713	37.593	845.60	398.6[1]
59.7	1.4438	34.795	792.57	397.8

TABLE XXVII.—BROMINE; M_{Br_2} = 159.84; t_c obs. = 302.2°.

0	3.1872	52.368	712.17	304.4

Ramsay and Aston, k_B = 2.1212.

t.	$w(M/d)^{2/3}$.	t_c.
10.6	552.08	276.9
46.0	487.98	282.1
78.1	426.09	285.0

TABLE XXVIII.—CARBON DISULFIDE; M = 76.14; $d_t = 1.29215 - 0.0013025t$; t_c obs. from 271.8°–279.6°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
20.13	1.2659	35.437	544.05	254.1

Morgan and Thomsen, t_c = 252.1; Ramsay and Shields, t_c = 270.2–271.7; Ramsay and Aston, t_c = 251.1, 257, 257.4.

TABLE XXIX.—CYMENE; M = 134.112; $d_t = 0.862 - 0.0008044$ (t—11.9°); t_c obs. = 378.6°.

18.7	0.8565	30.413	883.52	394.9
59.45	0.8235	26.330	785.20	394.5

[1] Miss C. M. Sillcox, working with a slightly smaller tip, and Miss J. Y. Cann with one larger as well as one smaller, have found since, at all temperatures, that t_c = 397.0°.

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Renard and Guye, $k_B = 2.1108$.

t.	$w(M/d)^{2/3}$.	t_c.	t.	$w(M/d)^{2/3}$.	t_c.
11.9	809.38	401.3	108.9	591.04	394.9
31.7	767.13	401.1	117.0	571.57	373.7
54.8	711.65	398.0	134.9	532.96	393.4
74.5	667.08	396.5	146.5	505.48	392.0
91.8	627.35	395.0	163.4	469.68	391.9
			172.8	451.50	392.7

Average, 395.5

TABLE XXX.—DIMETHYLANILINE; M = 121.1; $d_t = 0.9589-0.000825\ (t-16.7)$; t_c obs. = 414.45°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
21.5	0.95494	39.615	999.94	446.5
59.53	0.92360	34.900	900.74	442.9

Dutoit and Friederich, $k_B = 2.1012$.

t.	$w(M/d)^{2/3}$.	t_c.	t.	$w(M/d)^{2/3}$.	t_c.
22.7	891.5	453.0	76.7	762.5	445.6
43.5	838.6	448.6	99.0	708.3	442.1

Renard and Guye, $k_B = 2.1108$.

10.9	909.75	447.9	126.7	644.16	437.9
41.0	845.41	447.5	134.8	626.26	437.5
55.0	811.76	445.6	154.0	582.87	436.2
78.9	753.38	441.8	165.0	560.61	436.6
96.0	714.26	440.4	175.5	533.28	435.1
108.8	684.25	438.9			

TABLE XXXI.—DIPHENYLMETHANE; M = 168.1; $d = 1.0126-0.0007914\ (t-11)$; t_c obs. = 497°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
59	0.9746	37.80	1171.26	555.8

Dutoit and Friederich, $k_B = 2.1012$.

108.3	..	..	931.4	557.5
210.2	..	..	677.1	538.4

TABLE XXXII.—ETHYLBENZENE; M = 106.08; $d_t = 0.88316-0.0008333t$; t_c obs. = 463.4°.

21.0	0.86566	31.325	772.83	350.8
59.5	0.83358	26.775	681.13	351.3

TABLE XXXIII.—ETHYLANILINE; M = 121.098; $d_t = 0.9796-0.000831t$; t_c obs. = 425.4°.

35.8	0.9499	37.98	962.06	444.9
58.7	0.9310	35.35	907.51	445.0

Dutoit and Friederich, $k_B = 21.012$.

7.4	..	..	927.9	455.0
107.8	..	..	698.4	446.2
210.0	..	..	477.6	443.3

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TABLE XXXIV.—ETHYLENE CHLORIDE; M = 98.95; d_t = 1.28015–0.001528t; t_c obs. = 283.3° to 289.3°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
34.1	1.22805	33.178	618.79	299.5
60.0	1.18850	29.270	558.09	299.8

TABLE XXXV.—ETHYLIDENE CHLORIDE; M = 98.95; d_t = 1.207–0.0016t; t_c obs. = 250, 254.5, 260.0.

34.1	1.1524	26.043	506.87	252.5
56.9	1.1160	22.760	452.56	252.5

TABLE XXXVI.—TOLUENE; M = 92.064; d_t = 0.8682–0.000953 (t—15.2); t_c obs. = 320.7°.

36.0	0.8484	28.925	658.57	318.0
59.2	0.8263	26.075	603.75	318.2

Ramsay and Aston, k_B = 2.1212.

t.	$w(M/d)^{\frac{2}{3}}$.	t_c.	t.	$w(M/d)^{\frac{2}{3}}$.	t_c.
15.2	631.0	318.7	78.4	490.8	315.8
46.6	563.9	318.0	132.5	382.2	319.5

Renard and Guye, k_B = 2.1108.

13.1	630.65	317.9	79.0	490.01	318.1
29.1	596.87	317.9	91.5	464.48	317.5
48.0	555.29	317.1	108.9	431.21	319.2
59.0	532.93	317.5			

TABLE XXXVII.—PHOSPHORUS TRICHLORIDE; M = 137.38; t_c obs. = 285.5°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
35.6	1.5649	29.73	587.24	287.7

Ramsay and Shields, k_B = 2.1012

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
16.4	..	..	562.3	288.0
46.2	..	..	499.8	290.0

TABLE XXXVIII.—*p*-XYLENE; M = 106.08; d_t = 0.8801–0.0008468t; t_c obs. 344.4°.

37.9	0.8480	28.785	720.0	345.6
59.2	0.8300	26.308	667.51	344.9

TABLE XXXIX.—*o*-XYLENE; M = 106.08; d = 0.8932–0.0008425t; t_c obs. 358.3°.

23.85	0.8731	32.015	785.36	358.9
59.4	0.8432	27.880	701.07	359.2

TABLE XL.—*m*-XYLENE; M = 106.08; d_t = 0.8740–0.000944 (t—10); t_c obs. = 345.6°.

24.9	0.8599	30.38	752.86	346.4
58.9	0.8271	26.41	671.67	346.3

Dutoit and Friederich, k_B = 2.1012.

15.7	..	..	714.2	361.6
74.9	..	..	583.4	358.5
136.7	..	..	445.8	354.8

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Renard and Guye, $k_B = 2.1108$.

t.	$w(M/d)^{2/3}$.	t_c.	t.	$w(M/d)^{2/3}$.	t_c.
10.0	707.95	351.4	88.0	540.82	350.2
38.0	651.57	352.7	99.4	516.76	350.2
49.8	624.47	351.6	109.0	499.18	351.5
63.9	592.78	350.7	128.3	458.93	351.7
76.8	564.88	350.4	136.5	442.49	352.1

TABLE XLI.—METHYLANILINE; M = 107.08; $d_t = 0.9944-0.000801\ (t-10)$; t_c obs. = 428.6°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
24.6	0.9827	42.86	977.78	440.3
59.7	0.9546	38.38	892.68	439.7

Dutoit and Friederich, $k_B = 2.1012$.

9.9	..	..	886.5	437.8
108.5	..	..	690.2	443.0
210.8	..	..	477.7	444.1

TABLE XLII.—MESITYLENE; M = 120.1; $d_t = 0.8746-0.00081t$; t_c obs. = 367.7°.

23.5	0.8656	30.32	812.61	370.0
57.3	0.8282	26.60	734.21	370.9

Renard and Guye, $k_B = 2.1108$.

t.	$w(M/d)^{2/3}$.	t_c.	t.	$w(M/d)^{2/3}$.	t_c.
11.4	758.23	376.6	92.2	582.01	373.9
25.1	722.05	373.2	108.9	544.83	373.0
36.3	703.75	375.7	127.0	509.38	374.3
55.4	661.74	374.9	146.6	465.98	373.4
64.8	646.60	377.1	156.2	445.30	373.2
74.3	619.39	373.8			

TABLE XLIII.—ISOBUTYL ACETATE; M = 116.1; $d = 0.8802-0.001055\ (t-10)$; t_c obs. 288.3°, 295.8°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
23.8	0.8656	25.35	664.23	308.1
59.2	0.8282	21.55	581.54	309.0

TABLE XLIV.—IODOBENZENE; M = 203.96; $d_t = 1.8606-0.001535t$; t_c obs. = 448°.

t.	d.	w.	$w(M/d)^{2/3}$.	t_c.
23.5	1.8245	43.55	1010.62	453.0
59.6	1.7691	39.08	925.73	453.5

TABLE XLV.—FLUOROBENZENE; M = 96.04; $d_t = 1.0466-0.001208t$; t_c obs. = 286.6°.

9.3	1.0354	31.077	636.80	282.1
34.5	1.0049	27.537	575.62	281.7

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TABLE XLVI.

t_c = constant $\frac{\alpha' + \alpha''}{\alpha'\alpha''}$ $\quad w_t = w_o(1-\alpha' t)$ $\quad \frac{w_t}{d_o} = v_t = v_o(1-\alpha'' t)$.

Liquid.	α'.	α''.	t_c.	t_c from k_B.
Benzene	0.004078	0.003227	[288.5]	..
Constant from benzene = 0.51974				
Pyridine	0.003472	0.002678	344.0	..
Bromobenzene	0.003073	0.002423	383.6	398.2
Cymene	0.003103	0.002336	389.6	394.7
Ethylbenzene	0.003496	0.002747	337.9	351.0
Ethylene chloride	0.003934	0.003058	302.0	299.6
Ethylidene chloride	0.004654	0.003737	250.8	252.5
Ethylaniline	0.002729	0.002038	445.5	445.0
Dimethylaniline	0.002935	0.002233	409.8	444.4
Toluene	0.003670	0.002876	322.3	318.1
p-Xylene	0.003504	0.002783	335.1	345.3
o-Xylene	0.003332	0.002590	356.7	359.0
m-Xylene	0.003508	0.002613	347.1	346.4
Methylaniline	0.002775	0.002112	433.5	440.0
Mesitylene	0.003345	0.002307	380.7	370.5
Isobutyl acetate	0.003842	0.002928	312.8	308.5
Fluorobenzene	0.004338	0.003344	275.3	281.9
Iodobenzene	0.002665	0.001969	459.0	453.3

Discussion of Results.

The liquids studied above were of the greatest attainable purity. The bromobenzene and iodobenzene were especially prepared in this laboratory; the diphenylmethane was from Eimer and Amend, redistilled and recrystallized just before the determination was made; the isobutyl acetate, *m*-xylene, *o*-xylene, *p*-xylene, one sample of mesitylene, bromine and phosphorus trichloride were from Kahlbaum, usually redistilled just before using; while the others, including a sample of mesitylene, were especially prepared for this work by the Hoffman and Kropff Chemical Company,[1] and used directly. An idea of the purity of the latter preparations may be gained from the fact that the carbon disulfide possessed only the pleasant ethereal odor which characterizes the pure substance. The two samples of mesitylene, here, from the different sources, seemed to be perfectly interchangeable, no difference in drop weight being observable.

It will be noted that four liquids were studied at but one temperature, *viz.*: bromine, phosphorus trichloride, diphenylmethane, and carbon disulfide. In the case of carbon disulfide it was thought necessary to study only one temperature, to see if this undoubtedly pure sample would give a higher value of t_c than that found for another sample by Morgan and Thomssen, which might explain the considerably higher value of Ramsay and Shields, that could not be duplicated by Ramsay and Aston. As will be observed the value found, however, is only slightly larger than

[1] 619 Kent Ave., Brooklyn, N. Y.

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that of Morgan and Thomssen, showing this smaller value to be correct. With phosphorus trichloride difficulty was experienced at 60°, a yellow substance forming in the ventilation tube, due perhaps to the failure of the drying tubes to exclude water vapor. As the result at the lower temperature agreed with the observed critical temperature, and with that obtained at another temperature from capillary rise, no further determinations were made. The low temperature result for bromine was considered sufficient, since it practically agreed with the observed critical temperature, and the Ramsay and Aston figures by aid of capillary rise, which disagreed with it, were stated by the authors to be probably inaccurate. At low temperatures the diphenylmethane gave trouble, owing to spontaneous crystallization. As the capillary rise value at another temperature agreed with the 60° result; here, also, it was thought unnecessary to make further determinations.

Since the value of t_c is equal to the observed critical temperature in the case of bromine; and in those of phosphorus trichloride and diphenylmethane practically the same t_c is to be found from capillary rise at a different temperature of observation, *we can conclude that all the above liquids, with the exception of dimethylaniline, are normal in molecular weight, i. e., are non-associated; for all, with this exception, lead to the same calculated value of* t_c *(within a very small difference) at both temperatures of observation.*

In the case of dimethylaniline, the same trend is shown by drop weight as that observed in the results from capillary rise; but it is quite likely that this discrepancy in t_c of 0.8 per cent. between 21.5° and 59.5° is due to the decomposition of this very unstable liquid, which darkens very rapidly on exposure to light. Here the low temperature result was obtained first, when the liquid was fresh—possibly a reversed procedure would have shown a trend in the opposit direction. Whatever the cause, however, we cannot say from the results that the molecular weight is normal, although it is quite evident that if it changes with the temperature, the change is not very great.

The agreement of the calculated t_c *with the observed critical temperature is found to be very satisfactory for the following liquids: Bromine, bromobenzene, ethylidene chloride, toluene, phosphorus trichloride, p-xylene, o-xylene, and m-xylene, while for mesitylene, ethylbenzene and iodobenzene the discrepancies are below 1 per cent. for the former, and but slightly above that for the two latter.* For all the other liquids the calculated t_c, *i. e.*, the *fictitious* critical temperature, *viz.*: the point 6° below which, by the formula $w(M/d)^{2/3} = k_B (t_c - t - 6)$, $w(M/d)^{2/3}$ would become zero, is larger than the observed critical value for cymene, dimethylaniline, ethylene chloride, methylaniline, ethylaniline, isobutyl acetate, and diphenylmethane, while it is smaller only for carbon disulfide and fluorobenzene.

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It is possible to compare with these values of the calculated t_c the corresponding values found from capillary rise, and consequently to find indirect proof of the relationship, at the same temperature, $w : \gamma :: K_B : k_B$, for the following liquids only: carbon disulfide, cymene, dimethylaniline, diphenylmethane, ethylaniline, toluene, phosphorus trichloride, *m*-xylene, methylaniline and mesitylene. In the cases of toluene and phosphorus trichloride the agreement is practically perfect between the t_c values from drop weight and from capillary rise. With diphenylmethane, ethylaniline and cymene and methylaniline, a value of t_c at some temperature is always found which is equal to the one, constant, figure found at both temperatures from drop weight. In the case of the latter liquid, here, the large change found from capillary rise between 9.9° and 108.5°, when compared with the smaller one between 108.5° and 210.8°, would seem to indicate error somewhere in the capillary rise method. With dimethylaniline the trend is the same in all results, although it can hardly be said that the agreement in the capillary rise results is satisfactory—all this, however, including the trend, may well be due to the decomposition of this very unstable liquid. For cymene it will be noted that the mean of all the values of t_c from capillary rise 395.5° is in fair agreement with the constant drop weight value of 394.7°. For *m*-xylene the drop weight values are constant, but lower than either set from capillary rise, but as these latter agree only in that they give a higher value, and differ from one another more than the lower one does from that from drop weight, it would seem to indicate a possibility of error in the determination of capillary rise.

In Table XLVI are given the t_c values calculated by aid of the Walden relationship, which does not require a knowledge of the molecular weight. In 8 cases here the agreement with the values calculated from k_B is all that could be expected, but in the other 8 the variation is larger than is warranted, it is thought, by the experimental results. This would make it appear as if there are certain cases where this relationship does not hold satisfactorily.

In the next paper of the series a report will be made upon the work on some of the lower esters.

Conclusions.

The results of this research may be summarized as follows:

I. According to the new definition of normal molecular weight, *i. e.*, that the normal (benzene) constant k_B give for the liquid a constant value of t_c independent of the temperature of observation, t, in the relationship $w(M/d)^{2/3} = k_B (t_c - t - 6)$, the following liquids are to be regarded as perfectly non-associated as is benzene itself: bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, *p*-, *o*-, and *m*-xylene, mesitylene, ethylbenzene, iodobenzene, fluorobenzene, cymene, ethylene chloride,

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methylaniline, ethylaniline, isobutyl acetate, carbon disulfide, and diphenylmethane. In the case of dimethylaniline the discrepancy in the values of t_c is 0.8 per cent., which is much too great for an experimental error, and can show that the molecular weight is only slightly abnormal, which may well be due to the fact that this liquid is very readily decomposed.

II. Of the value of t_c calculated for the above liquids, those for bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, *o*-, *m*-, and *p*-xylene agree excellently with the observed values of critical temperature, while the disagreement with this value is below 1 per cent. for mesitylene, and but slightly above that for ethylbenzene and iodobenzene.

III. The agreement between the calculated values of t_c from drop weight and those from capillary rise, with the 11 liquids which have been studied by that method, is exceedingly good for toluene and phosphorus trichloride. In the other cases the mean of the t_c value from capillary rise agrees well with that for drop weight; and it is only for mesitylene and *m*-xylene that the values in mean from capillary rise disagree with those from drop weight. In the case of the latter liquid, however, this seems to mean little, as the values by two observers, although higher throughout, do not agree even fairly with one another.

IV. The values of t_c calculated by aid of the Walden relationship, without the aid of the molecular weight, in 8 cases (out of the 16 to which it could be applied) agree very well with those calculated from k_B, the variation in the others, however, indicating that probably this relationship is not as general as was at first thought.

LABORATORY OF PHYSICAL CHEMISTRY.

A MODIFICATION OF THE PERIODIC TABLE.

BY ELLIOT QUINCY ADAMS.

Received March 30, 1911.

This article is to set forth and discuss the theoretical basis of an arrangement of the periodic table of the elements.

The principal defect of the earlier forms of the table, those formulated by Mendeléeff, Lothar Meyer and others, was that they placed in the same "family," as entirely homologous, elements as dissimilar as sodium and silver.

The double periods, of sixteen columns, of the more recent tables are a recognition of the fact that the number of elements in the different horizontal rows, or periods, is not constant. In this way the table has been made complete up to xenon (130.2), all known elements of lower atomic weight being accounted for, and only one space in the table, that below manganese, being vacant. Of the elements following xenon, the first two, cesium and barium, are obviously homologous with rubidium

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and strontium, and will be placed below them, however the subsequent elements may have to be arranged, and the elements from tantalum to bismuth are completely homologous with those from columbium (niobium) to antimony.

The elements remaining fall naturally into two divisions: the rare earth metals—lanthanum, cerium, praseodymium, etc., with atomic weights intermediate between those of barium and tantalum—and the radio-active elements—uranium, radium, thorium, actinium and their decomposition products, with atomic weights greater than that of bismuth; that is to say, greater than that of any other element.

The question as to the place in the table for these elements can be answered from analogy with the preceding periods, as follows:

Most of the families—vertical columns—of the table contain only one element of each period, but in the iron family three elements enter at a time. The term "group of elements" will be used for this case.

The three elements of least atomic weight are, in order, hydrogen (1.008), helium (3.99) and lithium (6.94). The elements most resembling hydrogen in their chemical behavior are the alkali metals.

It follows that hydrogen and helium constitute the first period of the table and that the second period begins with lithium and ends with neon (20.2), the homolog of helium and the element just preceding sodium (23.00), which as the next homolog of lithium, begins the third period. In like manner the third period ends with argon (39.88), the fourth period extends from potassium (39.10) to krypton (82.92), the fifth from rubidium (85.45) to xenon (130.2), and cesium (132.81) begins the sixth.

The number of elements or "groups of elements" in the various horizontal rows, or periods, is respectively 2, 8, 8, 16 and 16 for the first five periods, and apparently more than 16 for the sixth.

These numbers it will be noticed are even and, in fact, powers of two. Further, each period contains homologs of the elements in the preceding period. The alternate periods introduce new families of elements.

The first period contains two elements whose homologs will not be adjacent in succeeding periods, symbolically $1 + 1$; the second period contains a homolog of hydrogen, three solid elements for which the product of atomic weight and specific heat is abnormal, three diatomic gases and a homolog of helium, that is, $1 + 3 + 3 + 1$; the third period contains homologs of the elements of the second period and may be divided into two groups of four families which will be separated in the next period, symbolically $4 + 4$; the fourth contains homologs of the elements of the third and in the middle eight new families, $4 + 8 + 4$.

The fifth period, if the yet undiscovered homolog of manganese be included, contains sixteen elements, or groups of elements, homologous

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with the preceding, of which the first, second, fifth, sixth, eighth to thirteenth are represented by homologs in the sixth period.

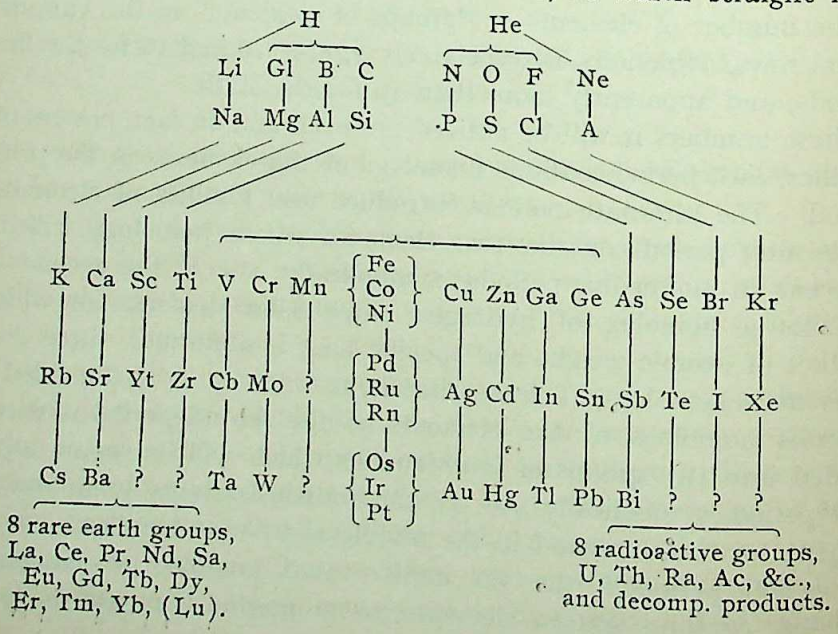
The arrangement of the groups of families in the preceding periods has been symmetrical, hence probably will be so in this period. If so the new families which appear in the sixth period will enter in two groups, the first being between barium and the homolog of yttrium or immediately after the latter. The number of families in the first group of families has been a power of two, or unity ($= 2^0$), in the preceding families, hence will in this case be two rather than three, symbolically, for the fifth period $2 + 12(?) + 2$, sixth $2 + x + 12 + x + 2$.

Inspection shows that in each of these symbolic expressions the g. c. d. of the terms is a power of two, and the quotient the expression resulting from raising the expression $(1 + 1)$ to some power by means of the binomial theorem, or:

Period.	Symbol.	Factors.
I	$1 + 1$	$1 \times (1+1)^1 = 2$
II	$1 + 3 + 3 + 1$	$1 \times (1+1)^3 = 8$
III	$4 + 4$	$4 \times (1+1)^1 = 8$
IV	$4 + 8 + 4$	$4 \times (1+1)^2 = 16$
V	$2 + 6 + 6 + 2$	$2 \times (1+1)^3 = 16$
VI	$2 + 8 + 12 + 8 + 2$	$\times (1+1)^4 = 32$

in which the number of elements in the period and the factor by which the appropriate power of the expression $(1+1)$ must be multiplied to obtain the division of the period into groups of families, alternately vary, both being powers of two.

The complete table of the elements follows, in which straight lines,



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vertical or inclined as the case may be, connect homologs. The arrangement of the rare earths, and of the radioactive elements, among themselves, remains to be done. These two groups of families lie in the same horizontal row with cesium and bismuth, and are careted in only to save space.

Exclusive of yet undiscovered rare earth or radioactive elements, the number of gaps remaining in the table is seven, the missing elements being homologous respectively to:

Yt, Zr, Mn (two elements), Te, I and Xe, with atomic weights respectively 173, 177, 100, 188, 212, 252± and 256±.

It is quite likely that lutecium (174.0) is identical with the first of these.

The rare earth metals at present known may be grouped as follows:

1	2	3	4	5	6	7	8
La 139.0	Ce 140.25	?	Sa 150.4	Gd 157.3	Dy 162.5	Er 167.4	Yb 172.0
	Pr 140.6		Eu 152.0	Tb 159.2		Tm 168.5	(Lu 174.0)
	Nd 144.3						

The atomic weights of the radioactive elements are not yet known accurately enough to serve as a basis for separation into groups and the number of radioactive elements is still uncertain.

It will be seen that one or more elements at the right hand end of each period are gaseous. Regarding *bromine* as a gas and leaving out of account the radioactive *emanations*, the following interesting relation obtains:

Period No.	No. of elements.	No. of gases.	Ratio.
I	2	2	1
II	8	4	$^1/_2$
III	8	2	$^1/_4$
IV	16	2	$^1/_8$
V	16	1	$^1/_{16}$
VI	32	(1)	$^1/_{32}$

This relation is suggestive rather than significant, for the physical state of an element is dependent on temperature and pressure, and normal temperature and pressure are, so to speak, "accidental."

It is to be remarked that variation in valence from odd to even and color in simple compounds are practically unknown in the eight families represented in the second period, while both are the rule in the group which enters in the fourth period, and to some extent with the rare earth and radioactive elements. Whether these two phenomena are related in any other way than in their being found in the same parts of the table remains to be proved, but by the electron theory such other connection is very probable, since each requires one or more electrons whose connection with the atom differs from that of the normal electron.

The use of the term "radioactive elements" for the elements of atomic weight greater than that of bismuth is not intended to imply that no

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other elements are at all radioactive, although all the elements for which radioactivity has been observed do lie in the group in question. The term is used rather as the term "magnetic elements" would be applied to iron, cobalt and nickel.

The exponents for the expression $(1+1)$ in the first table fall to unity in the third period, as in the first, suggesting that the first two periods belong to one part of the table and the remaining periods to another, with some parameter different in the two parts, a difference which ought to show in the equations for the spectra of the elements. In fact, while the equations for the spectral series are similar in form for hydrogen and all the alkali metals, the lines of the last four are double, whereas those of hydrogen and lithium are single, so far as is known.

The answer to the question as to the possibility of other periods awaits a more thorough knowledge of the theoretical basis of the relation between properties and atomic weights. At the same time the sequence of coefficients in the first table suggests that the coefficients for the period before that of hydrogen and that after the sixth would be zero. If this is true, it probably means that elements of atomic weight greater than 256 or less than 1 do not exist.

Summary.

The elements can be arranged in six periods, each including *some power of two* elements, or groups of elements.

The natural divisions of each period are some power of two times the coefficients of some binomial expansion, $(1 + 1)^n$.

Each period contains homologs of all the elements of the preceding period.

Several new families of elements appear in alternate periods.

The rare earths proper, and the radioactive elements are not homologous to any previous elements, but are two groups of families which enter with the sixth period.

Aside from rare earth and radioactive elements, seven elements remain to be discovered.

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[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

AURIC HYDROXIDE FORMED ON A GOLD ANODE. DEPORTMENT OF AURIC HYDROXIDE WHEN HEATED.

BY W. G. MIXTER.

Received March 20, 1911.

The writer was led to attempt the preparation of auric oxide by the electrolytic method for the purpose of using it in a determination of the heat evolved when it unites with sodium oxide. The investigation of

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the auric hydroxide formed when gold is the anode in an electrolyte has yielded interesting results. The difficulties in obtaining auric hydroxide and auric oxide free from metallic gold will be seen in the descriptions of the preparations.

A number of investigators have observed the corrosion of gold anodes. Grotthus mentioned it in 1806; later Bunsen observed that gold solder on a platinum electrode was attacked. Victor Lenher[1] in 1904 in studying the action of different oxidizing agents on gold found that a gold anode in a neutral solution of potassium or sodium sulfate or nitrate is attacked and that a little gold passes into solution. He stated that auric oxide is formed but gave no analysis. Rundespaden[2] analyzed a product which he prepared by a similar method with the following results:

		Calculated for $Au_2O_3.3H_2O$.
Gold	81.20	79.47
Oxygen	9.09	9.62
Water	9.80	10.91
	100.00	100.00

He did not state the atomic ratio of the gold to the oxygen in the substance which is 1 to 1.38 instead of 1 to 1.5 required by the formula Au_2O_3.

Preparation A.—The electrolyte was 2 liters of a saturated solution of potassium sulfate in a large wide beaker. The electrodes were gold and were suspended in two small beakers standing on the bottom of the large beaker. The object of this arrangement was to keep particles of gold dropping off the cathode from mixing with the auric hydroxide falling from the anode. A current of 3 amperes and 14 volts was used, giving a current density on the anode of about 0.3 ampere per square centimeter.[3] The electrolysis was continued six days and the water lost by evaporation was replaced from time to time. The apparatus was protected from light, but this precaution was found later to be unnecessary. A thin film of gold was deposited on the three beakers. The anode lost 9 grams and 2.3 grams of gold were found mostly on the cathode. On shaking up the auric hydroxide contained in the small beaker in which the anode was suspended thin yellow scales and white gelatinous particles were noticed. These were floated off and the washing by decantation with cold water was repeated a number of times after the wash water gave no turbidity when barium chloride was added. The auric hydroxide was dried in a partial vacuum over sulfuric acid, but not to a constant weight. It was found to contain gold 82.9, oxygen 10.0, potassium oxide 2.5, sulfur

[1] THIS JOURNAL, 23, 550 (1904).

[2] *Ann.*, 151, 339.

[3] No attempt was made to learn the best conditions as regards current density and voltage for the formation of auric hydroxide. It was, however, observed that the yield was very small when a current density of perhaps 0.03 ampere was used.

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trioxide 0.4 and water 4.2 per cent. The atomic ratio of the gold to the oxygen given off on heating is almost exactly 1 to 1.5. Next, 7 grams of the auric hydroxide were placed in a bulb tube having a capacity of 8 cc. and heated gradually in an electric furnace to 190°. After weighing, it was heated for two hours to 208–210°. It lost 2 mg. in weight. Finally the tube was connected by a capillary tube with a eudiometer and the gas was collected which came off between 205° and 220°. The latter temperature was maintained for $2^1/_2$ hours. The loss in weight in this last period of heating was 17 mg., and the gas collected 9.5 cc. or about 10 mg. of oxygen and 7 mg. of water driven off. The analysis of *A* heated as described gave:

	Per cent.	Atomic ratio.
Gold	85.0	1
Oxygen	10.0	1.46
Potassium oxide	2.5	
Sulfur trioxide	0.4	
Water by difference	2.0	
	100.00	

The method used in the analysis was as follows: A weighed portion of the substance was dissolved in hydrochloric acid, which left a little metallic gold, and the gold in solution was separated by sulfurous acid. In the filtrate from the gold the potassium was determined as sulfate. Another portion of the substance was dissolved in hydrochloric acid, the gold precipitated by ammonium oxalate, and in the filtrate from the gold sulfur trioxide was determined as barium sulfate. For the determination of oxygen the substance was placed by means of a small funnel tube in the bottom of a hard glass tube 6 inches long and 4 mm. internal diameter. Then the middle of the tube was drawn out and bent so as to make a narrow delivery tube. Next the tube with substance was placed in a narrow porcelain tube wound with platinum wire. The wire was connected with a circuit of four 32 candle power lamps. The heating was very gradual to prevent a violent evolution of gas. The oxygen was collected in a eudiometer graduated to 0.1 cc. The part of the tube heated had a volume of about 0.6 cc. and the allowance for expansion was 0.3 cc., which was deducted from 43.4 cc. of gas obtained.

Preparation B.—Electrolyte, 2 liters of 0.1 *N* sulfuric acid; anode, in small beaker standing in large beaker; cathode, a strip of gold near the top of the solution and on the opposit side of the large beaker from the anode; time of electrolysis, 4 days; anode lost 9.8 grams of gold. Only the auric hydroxide which collected in the small beaker was used. It was washed with cold water and dried in a partial vacuum but not to constant weight. It left a little gold when treated with hydrochloric acid, showing the presence of free gold in the substance; 10.330 grams of it were heated

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gradually to 205°, then the temperature rose during $3^1/_2$ hours to 215°. Next it was heated for an hour and a half from 207° to 235°. In this last heating the loss was 40 mg. and the total loss was 0.657 gram. An analysis gave gold 88.97 and oxygen 9.52 per cent., giving an atomic ratio of 1 to 1.35. It contained a little sulfur trioxide in combination, the amount of which was not determined.

Preparation C.—This was a repetition of *A* with this modification: the cathode, was placed in an inverted funnel tube designed to carry the hydrogen evolved out of the solution. Potassium hydroxide accumulated about the cathode, leaving the solution about the anode strongly acid. The auric hydroxide was mixed with white particles which could not be floated off, but which dissolved when the hydrate was treated with hot dilute nitric acid. On washing with hot water a little gas came off. The product, dried at 100°, was nearly free from sulfate and potassium but contained nitrate.

Preparation D.—The object was to learn whether or not nitric acid would answer for an electrolyte. The apparatus was arranged as described in *C*. A solution of 175 cc. of concentrated nitric acid in $2^1/_2$ liters of water was used. After the electrolysis had continued for some time the solution in the funnel tube about the cathode was strongly ammoniacal. The auric hydroxide which formed on the anode in the previous experiments was at first bright red and later a reddish brown, but in this test the oxidation product was yellowish brown. After washing, drying and heating to 220° it was a dark brown powder mixed with yellow particles. The atomic ratio of the gold to the oxygen found was 1.01 to 1.00. This was undoubtedly accidental, since the substance was not homogeneous. It was found that auric oxide and hydroxide are reduced by nitrous acid and this reaction accounts for the presence of considerable free gold in the above product, since nitrous acid is formed in the electrolysis of nitric acid.

Preparation E.—The electrolyte was a saturated solution of potassium sulfate; the cathode was in a porous porcelain cell standing in the solution; on the top of the cell was an inverted funnel to carry off the hydrogen. During the electrolysis, in which potassium hydroxid accumulated about the cathode, the alkaline solution flowed gradually over the top of the cell carrying a gelatinous compound. This was collected, washed moderately by decantation and was found to be soluble in dilute hydrochloric, sulfuric and nitric acids. A solution of it was evaporated and the residue obtained when treated with acid and water left silica. The red product of the electrolysis was digested with hot dilute nitric acid to remove the white substance mixed with it. When washing it with hot water minute bubbles of gas appeared. It was dried at 100° and then slowly heated to 200°. The ratio of the gold to oxygen found was 1 to 1.435.

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Preparation F.—The apparatus was the same as that used in the previous experiment and the electrolyte was 10 cc. of sulfuric acid in $2^1/_2$ liters of water. When the electrolysis had become very slow, owing to the removal of acid from the cell, solid potassium sulfate was added to the cell and more was put in from day to day. The auric hydroxide obtained was digested with hot dilute nitric acid to remove the white substance mixed with it and then washed with hot water. A very little gas came off from the auric hydroxide in the hot water. It was dried at 100° and then heated slowly to 204°. The atomic ratio of the gold to the oxygen found was 1 to 1.434. The substance which was heated to 204° gained in weight slowly when exposed to the air of the laboratory and rapidly in air saturated with water vapor, the weight becoming constant in eleven days. The total gain was 10.5 per cent. After standing four days over sulfuric acid the weight was only 0.05 per cent. greater than the original weight. The hygroscopic character of the substance is due to the porous condition which it shows under the microscope.

Preparation G.—The preceding experiments have shown that sulfuric acid is the best electrolyte to use in the preparation of auric hydroxide, and that hydrogen should be kept from the solution about the anode, and also that the silicic acid or silicate formed should not mix with the auric hydroxide. For this purpose the apparatus shown in Fig. 1 was used. The porous cell *c* was fitted by asbestos packing to a glass prolong. The tube *e* was connected with an exhaust and served to keep the solution in *c* a little below the level of that in *b*. The siphon *a* supplied water to *b* from the water in the large porcelain vessel. The cover *d* was to keep out dust. Water, $2^1/_2$ liters, and 5 cc. of sulfuric acid were placed in the jar *b*, and 30 grams of potassium sulfate were put into *c*, which was then filled with water. The current used was what passed from four 32-candle power lamps. It is understood that sulfate ions passed out of the cell and made the acid solution stronger. About a liter of water passed each day during the electrolysis into the cell and diluted the solution of potassium sulfate

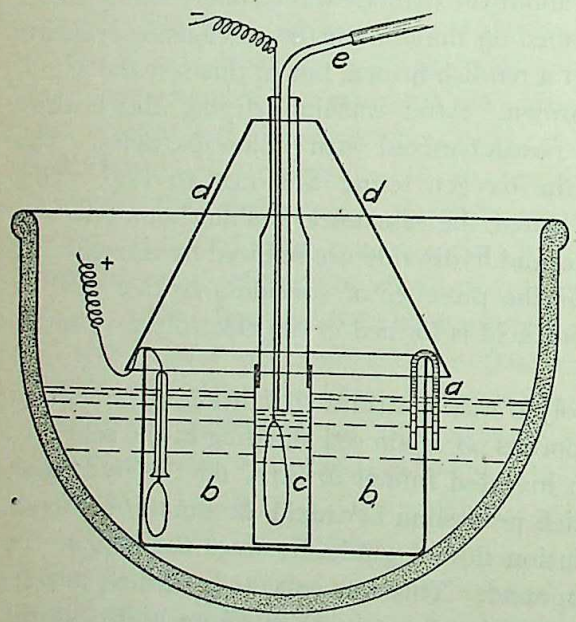


Fig. 1.

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and hydroxide. Hence it was necessary to add potassium sulfate from time to time.

The auric hydroxide obtained in the apparatus described was washed with cold water and dried in a partial vacuum over sulfuric acid. It was completely soluble in cold, dilute hydrochloric acid. The analysis gave the following results:

	Per cent.	Atomic ratio.
Gold	84.18	1
Oxygen given off on heating	10.17	1.488
Sulfuric oxide combined with gold oxide	0.26	
Water	5.51	
	100.12	

Krüss in an experiment to which reference is made later in this paper observed that auric hydrate on long heating at 160–170° ceases to lose in weight and that Au_2O_2 results. The auric hydroxide of the experiments preceding *G* did not yield this oxide on heating to 200° or higher, nevertheless it was thought best to try the effect of heating a longer time than heretofore. For this object the auric hydroxide was heated in a bulb and the results were as follows:

No. of expt.	Hours.	Temperature.	Weight of substance. Grams.
			3.6907
1	4	135°	3.6127
2	18	135–148	3.5615
3	3	160–178	3.5590
4	20	161–168	3.5507
5	6	161–170	3.5392
6	3	161–170	3.5307
7	24	180–204	3.504
8	$2^1/_2$	200–215	3.497
9	2	218–231	3.479
10	2	235–244	3.417
11	2	235–252	3.363
12	3	240–260	3.251
13	$2^1/_2$	250–295	3.126
		above 360	3.083

The loss in heating for 82 hours from 135° to 213° was 5.7 per cent. or practically the same as the per cent. of water in the substance. If one-third of the oxygen and all of the water had been driven off the loss would have been 8.9 per cent.



Fig. 2.

To learn whether or not auric hydroxide is decomposed by light 0.143 gram was placed in the closed end of the tube, Fig. 2, and the lower bend was sealed with mercury. The temperature of the tube and atmospheric pressure were noted. After two weeks' exposure to direct sunlight the

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volume of air in the tube and the color of the hydroxide were unchanged, showing that dry auric hydroxide is not decomposed by light.

Preparation H.—About 16 grams of auric hydroxide were prepared and washed as described in *G*. It was a dark red substance mixed with a small amount of dull yellow matter which was not free gold because it was soluble in hydrochloric acid. The substance, dried for three days in a partial vacuum over sulfuric acid, was found to have the composition of auric trihydrate; over 8 grams of this hydrate were heated for three days to 157–166°; losing in weight only 12 mg. on the second and the same on the third day. After this heating it was completely soluble in hydrochloric acid and an analysis of it gave: gold, 86.50; oxygen, 10.57; sulfur trioxide, 0.25; water by difference, 2.68 per cent. The atomic ratio of the gold to the oxygen is 1 to 1.51. This sample of auric hydroxide having 2.68 per cent. of water was next heated for 3 hours to 200–210°. It lost oxygen but retained water as the following analysis shows:

				Atomic ratio.
Gold		87.21	87.2	1
Oxygen	10.23	10.18	10.2	1.44
Sulfur trioxide		0.25	0.25	
Water by difference			2.35	
			100.00	

Preparation I.—About 6 grams of auric hydroxide described above were dissolved in 75 cc. of hot concentrated nitric acid and the solution was evaporated to about 50 cc. The slight amount of insoluble substance was removed by filtering the solution through asbestos. The clear solution was next poured into a liter of water. After the auric hydroxide had settled the supernatant liquid was decanted and then boiling water was added and the whole boiled for an hour. This was repeated again, but afterwards boiling water was added to the precipitate but the whole was not again boiled. The washing by decantation was repeated six times in as many days and about 10 liters of water were used. Finally the auric hydroxide was collected on a hardened filter, washed with hot water and dried in a vacuum over sulfuric acid. Next 2.3042 grams were heated 44 hours at 158–167° and then analyzed with the following results:

		Atomic ratio.
Gold	86.7	1
Oxygen	10.6	1.50
Water and NO_3 by difference	2.7	
	100.00	

Preparation J.—Various residues of auric hydroxide were dissolved in hot sulfuric acid. The solution was filtered through asbestos and poured into water. After boiling a short time the precipitate was allowed to

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settle, then collected on a filter and washed with hot water. Next it was placed in $1^1/_2$ l. of water, which was then boiled an hour and left over night in a steam bath. It was collected on a filter again and washed with hot water. After drying over sulfuric acid 0.8457 gram of the substance was found to contain gold, 84.0, and SO_3, 0.003 per cent. Next 4.1147 grams of the compound were heated 68 hours at 160–172°, losing 3.3 mg. in the last 20 hours. An analysis at this stage of the heating gave:

		Atomic ratio.
Gold	87.1	1
Oxygen	10.4	1.48
Water by difference	2.5	
	100.0	

The remainder of the auric hydroxide, which contained 2.5 per cent. of water, was heated 12 hours at 173–187° and 24 hours at 203°, losing 1.5 mg. the last hour. The substance then contained: gold, 91.7; oxygen, 7.0; water by difference, 1.3 per cent. Water was undoubtedly present, as it appeared in the colder part of the tube when the substance was heated to drive off oxygen in the analysis. The atomic ratio of the gold to the oxygen is nearly 1 to 1, but this is not significant, since the substance had not attained a constant weight at 203°. Finally the substance was heated for 96 hours to 211–222°, and 24 hours to 235–240°, losing during this last heating of 24 hours 0.5 per cent. in weight.

The following table shows the results obtained with the different preparations of auric hydroxide.

Preparation.	Electrolyte.	Hours heated.	Temperature.	Ratio after heating Au : O.	% of water after heating.	Remarks.
A...	K_2SO_4	..	20°	1 : 1.5	4.2	Dried over sulfuric acid.
		4	220	1 : 1.46	2.0	
B...	H_2SO_4	4	205–235	1 : 1.35	2.3	
D...	HNO_3	*	220	1 : 1	**	Contained gold reduced by HNO_2.
E...	H_2SO_4	*	200	1 : 1.43	**	*Heated slowly to temperature given.
F...	H_2SO_4	*	204	1 : 1.43	**	**Contained water after heating.
G...	H_2SO_4	..	..	1 : 1.49	5.5	Dried over sulfuric acid.
		82	135–231	..	..	Lost weight constantly.
H...	H_2SO_4	72	157–166	1 : 1.51	2.7	
		3	200–210	1 : 1.44	2.3	
I....	..	44	158–167	1 : 1.5	2.7	From hydrolysis of nitrate.
J...	..	68	160–172	1 : 1.48	2.5	From hydrolysis of sulfate.
		36	173–203	1 : 1	1.3	

We observe that auric hydroxide does not lose oxygen on long heating at 160–170°; at higher temperatures it gives off oxygen slowly but retains

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water above 200°; These results differ essentially from those of two other investigators whose work is quoted in some detail for discussion later. Schottländer,[1] by the hydrolysis of auric sulfate, prepared auric hydroxide of the following compositions:

	Calculated for $Au_2O_3H_2O$.	Found.
Au	85.63	84.86
O	10.45	10.44
H_2O	3.92	4.20
SO_3	..	0.58
	100.00	100.00

He mixed 1.1847 grams of the preparation in a tube with dry sodium carbonate, passed dry air over the mixture and through a calcium chloride tube. The substance lost water and oxygen on heating as follows:

3	hours at 106°	0.0155 gram	= 1.31 per cent.
2½	hours at 141–145°	0.0188 gram	= 1.59 per cent.
2½	hours at 176–180°	0.0101 gram	= 0.92 per cent.
2	hours at 205–205°		0.38 per cent.
			Water, 4.20

The loss of oxygen was for:

3	hours at 205–208°		0.21 per cent.
1½	hours at 245–251°	0.1098 gram	= 9.27 per cent.
½	hour at dull red	0.0157 gram	= 1.32 per cent.
			Oxygen, 10.80

Krüss[2] prepared auric hydroxide by adding magnesia to a solution of the chloride, digesting the precipitate with nitric acid to remove magnesia and then treating the residue with hot water to remove nitric acid. The auric hydroxide was free from magnesia and nitric acid. His observations of the deportment of the auric hydroxide on prolonged heating are as follows:

No. of expt.	Hours.	Temperature.	Weight of substance. Grams.
1	10	110–120°	1.6550
2–4	15	110–150	1.6258
5–6 (water-free)	34	140–150	1.5632
7–10	26	150–173	1.5579
11–15	11	170–200	1.4689
18	6	225–235	1.4421
20	½	red heat	1.4420

The weight was constant in the seventh, eighth, ninth and tenth experiments and from this weight and the weight of the gold left Krüss derived the formula Au_2O_2.

[1] *Ann.*, 217, 312.
[2] *Ibid.*, 237, 294.

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The writer found that the auric hydroxide of preparation *G* did not attain constant weight on heating 52 hours at 160–178°; that preparations, *H*, *I* and *J* after heating for 72, 44 and 68 hours respectively to 157–172° were essentially auric oxide with 2.5 to 2.7 per cent. of water; *H* and *J* at higher temperatures lost oxygen but did remain constant in weight at any temperature, nor become anhydrous at 200–210°, that is, none of the preparations gave on heating auric oxide, Au_2O_3, indicated by the one experiment by Schottländer, or the auroauric oxide, Au_2O_2, derived from the data of one experiment by Krüss. The former did not heat, as Krüss[1] suggests, a sufficient length of time to expel the water from the hydrate. Moreover, the writer has shown, as stated, that water is retained at 210°. Krüss's result would have been more satisfactory if he had measured the oxygen given off by what he regarded as Au_2O_2 instead of calling the loss in weight oxygen. While he did the work with great care the existence of Au_2O_2 is doubtful.

The compound formed on a gold anode is auric hydroxide with varying amounts of water, three molecules or less. When potassium sulfate is the electrolyte a notable quantity of potassium is retained by the hydroxide, presumably as an acid potassium aurate. With sulfuric acid for an electrolyte the product contains a little basic auric sulfate which is not removed by cold water. Since ozone does not attack gold, the corrosion of the metal is not due to the ozone formed in the electrolysis, and it is probable that auric sulfate is formed by the union of sulfate ions with gold, the auric sulfate hydrolyzing at once in the dilute acid solution. The auric hydroxide formed on a gold anode under the microscope is ruby-red in color, translucent, and appears to be an aggregation of minute particles with curved surfaces. Some flat surfaces are seen which indicate crystallin structure. The anodic hydroxide and the amorphous form obtained by hydrolysis of auric nitrate or sulfate behave essentially alike when heated and neither yields auroauric oxide, Au_2O_2, or auric oxide, Au_2O_3. Auric hydroxide is reduced to the metal by hydrogen peroxide and by a solution of sodium peroxide. It may be mentioned that a fulminate forms on a gold anode in a solution of ammonium carbonate.

[Contribution from the Chemical Laboratory of the University of Cincinnati.]

NOTES ON THE PREPARATION OF CHROMYL COMPOUNDS.

By Harry Shipley Fry.

Received February 24, 1911.

The present paper is a résumé of some work, the object of which was the preparation of the unknown compounds, chromyl bromide and chromyl iodide. While it was only partially successful in this respect, certain note-

[1] *Loc. cit.*

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worthy results were obtained, namely: a new reaction for the preparation of chromyl chloride; a reaction for the detection of minute traces of chromyl chloride (0.0000[illegible]1 g. per 1 cc. of solvent) depending upon the formation and color of chromyl bromide; the preparation and identification of the new compounds, anhydrous chromic acetate and chromyl acetate.

The interaction of the halide and the dichromate of a metal with an excess of concentrated sulfuric acid constitutes the general method of preparing either chromyl fluoride or chloride. The chromyl halide thus prepared is specifically a product in the reversible reaction represented by the equation

$$(HO)_2CrO_2 + 2HX \rightleftarrows CrO_2X_2 + 2H_2O. \quad (X = Cl \text{ or } F.)$$

The appropriation of the water by the excess of concentrated sulfuric acid prevents hydrolysis and thus renders possible the recovery of the chromyl halide by distillation.

This method cannot be extended to the preparation of chromyl bromide or iodide, since the intermediately formed hydrobromic or hydriodic acid is susceptible to oxidation by chromic and by sulfuric acid and thereby yields free bromine or iodine respectively. It follows, therefore, that a general reaction for the preparation of the chromyl halides should be conducted in anhydrous solvents and avoid the formation of halogen acids in the presence of oxidizing agents. The first reaction investigated from this standpoint was that of anhydrous potassium chromate upon acetyl chloride dissolved in carbon disulfide.

Interaction of Potassium Chromate and Acetyl Chloride.—Several reactions are theoretically possible as indicated in the following equations:

(1) $2CH_3COCl + (KO)_2CrO_2 = 2CH_3COOK + CrO_2Cl_2$;

(2) $2CH_3COOK + CrO_2Cl_2 = (CH_3COO)_2CrO_2 + 2KCl$;

(3) $2CH_3COCl + (KO)_2CrO_2 = (CH_3COO)_2CrO_2 + 2KCl$.

The feasibility of the first reaction would warrant its extension to the preparation of chromyl bromide or iodide by employing acetyl bromide or iodide respectively. The interaction of the products of equation (1), according to equation (2), would result in the production of a new compound, acetyl chromate or chromyl acetate, the name respectively depending upon whether the substance is regarded as a derivative of chromic acid or of acetic acid. The possibility of the direct formation of chromyl acetate is indicated in equation (3).

One-half gram-molecular quantities (according to equation 1) of anhydrous potassium chromate and acetyl chloride, in 500 cc. of anhydrous carbon disulfide, were heated to boiling upon a water bath in a flask provided with reflux condenser. Apparently no reaction took place until a few drops (1 cc.) of glacial acetic acid were added, whereupon the mix-

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ture immediately assumed a deep red color (due to the formation of chromyl chloride) and boiled spontaneously for an hour. The contents of the flask were then poured into a Büchner filter and thoroughly washed with carbon disulfide. Aliquot portions of the filtrate, when shaken with water, yielded aqueous solutions of chromic acid which upon titration with standard ferrous ammonium sulfate solution gave the equivalent content of chromyl chloride. The quantity of chromyl chloride in the distillate was thus found to equal 3.83 per cent. of the theoretical yield required by equation (1).

The contents of the filter consisted almost entirely of unaffected potassium chromate completely covered over with a brown substance insoluble in carbon disulfide. Consequently its formation prevented complete interaction between the potassium chromate and the acetyl chloride, thereby accounting for the low yield of chromyl chloride. An aqueous solution of this brown substance gave reactions for hydrogen, acetate, and chromate ions, which would be the naturally expected products of the hydrolysis of chromyl acetate as indicated in the equation

$$(CH_3COO)_2CrO_2 + 2HOH = 2CH_3COOH + (HO)_2CrO_2.$$

Either of the above noted equations, (2) or (3), would account for the formation of chromyl acetate. The preparation of chromyl acetate through the interaction of silver acetate and chromyl chloride (to be described later) is analogous to the reaction represented by equation (2), and serves to substantiate the above assumption.

It has been noted that the interaction between acetyl chloride and potassium chromate did not occur until a few drops of acetic acid were added. Hence it is possible that the acetic acid functions catalytically according to the equations:

$$2CH_3COOH + (KO)_2CrO_2 \longrightarrow 2CH_3COOK + (HO)_2CrO_2,$$
$$(HO)_2CrO_2 + 2CH_3COCl \longrightarrow CrO_2Cl_2 + 2CH_3COOH.$$

The generation of free chromic acid would, accordingly, precede and condition the formation of chromyl chloride. Furthermore, the interaction of any given acetyl halide with chromic acid should result in the formation of the corresponding chromyl halide.

Interaction of Chromic Acid and Acetyl Chloride.—When a solution of acetyl chloride in carbon tetrachloride is added to dry pulverized chromic anhydride no change is apparent; but when a few drops of glacial acetic acid are added, the chromic anhydride dissolves with the evolution of heat, and a dark red solution of chromyl chloride is formed. The equations for the reactions involved are presumably as follows, the acetic acid functioning as a catalytic agent:

$$CrO_3 + 2CH_3COOH \longrightarrow (HO)_2CrO_2 + (CH_3CO)_2O;$$
$$(HO)_2CrO_2 + 2CH_3COCl \longrightarrow CrO_2Cl_2 + 2CH_3COOH.$$

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One-eighth gram-molecular quantities of chromic anhydride and acetyl chloride, plus an excess of 10 grams of the latter reagent, in 100 cc. of carbon tetrachloride, to which was added 1 cc. of glacial acetic acid, were heated together upon a water-bath in a half-liter flask equipped with reflux condenser. When the chromic anhydride was dissolved the condenser was turned down and the contents of the flask subjected to distillation. For every 50 cc. of distillate collected there was added to the distilling flask 50 cc. of carbon tetrachloride. In this manner the chromyl chloride was completely driven over into the distillate, the total volume eventually amounting to 500 cc. Aliquot portions of the distillate on treatment with water and subsequent titration with standard ferrous sulfate solution gave data calculating to a yield of 15.96 grams of chromyl chloride, or 82.43 per cent. of the theoretical based upon the ratio CrO_3: CrO_2Cl_2. The separation of chromyl chloride from the solvent carbon tetrachloride by fractional distillation is practically impossible. The solid dark green residue in the distilling flask, weighing 8.50 grams, consisted chiefly of chromic acetate and chloride.

The interaction of chromic acid and acetyl chloride thus affords a new method of producing chromyl chloride. Analogously, chromic acid and acetyl bromide should, presumably, yield chromyl bromide.

Interaction of Chromic Acid and Acetyl Bromide.—When 12.5 grams of chromic anhydride were added to a solution of 41.0 grams of acetyl bromide in 100 cc. of carbon tetrachloride, containing 1.0 cc. of glacial acetic acid, a singular transition of colors was noted. An intense permanganate-red coloration appeared and then faded rapidly to red-brown. Treatment of the reaction mixture as described in the above preparation of chromyl chloride yielded a red distillate, the color of which vanished upon treatment with potassium hydroxide solution. The red color of the distillate was therefore due to bromine and not to any volatil chromyl compound. The quantity of bromine was determined by titrating aliquot portions of the distillate with standard sodium arsenite solution and thus found to equal 4.98 grams, or 25 per cent. of the theoretical yield based upon the assumption that chromyl bromide was formed ntermediately, thereby producing the permanganate-red coloration, and then decomposed yielding the red-brown solution of free bromine. The solid green residue remaining n the distilling flask weighed 30 grams and upon analysis was found to contain 27.72 per cent. of unaffected chromic anhydride; 12.78 per cent. of chromium, combined as acetate and bromide; and 25.60 per cent. of combined bromine.

Chromyl Bromide.—The possibility of the production of chromyl bromide as an unstable compound yielding solutions of characteristic color is supported by four different reactions:

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(1) If a solution of anhydrous hydrogen bromide in carbon tetrachloride is added to a small quantity of dry chromic anhydride the solution immediately assumes a permanganate-red color, which slowly fades to orange-red:

$$CrO_3 + 2HBr = CrO_2Br_2 + H_2O.$$

(2) The addition of a carbon tetrachloride solution of hydrogen bromide to a very dilute solution of chromyl chloride produces an intense permanganate-red coloration which gradually fades to orange-red:

$$CrO_2Cl + 2HBr = CrO_2Br_2 + 2HCl.$$

(3) The interaction of chromic anhydride and acetyl bromide in the presence of glacial acetic acid, as described above, may be represented by the equation

$$(HO)_2CrO_2 + 2CH_3COBr = CrO_2Br_2 + 2CH_3COOH.$$

(4) The addition of one drop of acetyl bromide to five cc. of a solution prepared by dissolving one drop of chromyl chloride in 500 cc. of carbon tetrachloride is also productive of the permanganate-red color, which vanishes in the course of five minutes:

$$CrO_2Cl + 2CH_3COBr = CrO_2Br + 2CH_3COCl.$$

The delicacy of this last reaction as a color test for minute traces of chromyl chloride (0.00001 gram per 1 cc. of solvent) was determined as follows: Solutions of chromyl chloride in carbon tetrachloride were prepared containing, per cubic centimeter, 0.01, 0.001, 0.0001 and 0.00001 gram of chromyl chloride, and numbered 1 to 4 respectively. Twenty-nine cubic centimeters of each of these solutions were placed in Eggertz tubes and to each was added one cubic centimeter of pure acetyl bromide. The colors of the solutions in the Eggertz tubes both before and after the addition of acetyl bromide are tabulated in terms of Mulliken's Color Standards[1] as follows:

Concentration of CrO_2Cl_2 solution.	Color before addition of CH_3COBr.	Color after addition of CH_3COBr.
(1) 1 cc. = 0.01 g.	Normal O R.	Violet-black.
(2) 1 cc. = 0.001 "	" R O.	Normal R.
(3) 1 cc. = 0.0001 "	" O Y.	Tint 1, V R.
(4) 1 cc. = 0.00001 "	Tint 2, Y.	" 2, O R.

Solutions of chromyl chloride have the color of bromine solutions while solutions of chromyl bromide are identical in color with solutions of iodine in such solvents as carbon disulfide, chloroform, and carbon tetrachloride.

Interaction of Chromic Acid and Acetyl Iodide.—The interaction of chromic acid and acetyl iodide was investigated in precisely the same manner as were the reactions with acetyl chloride and bromide. There was no direct evidence of the formation of chromyl iodide. The distillate contained free iodine in quantity equivalent to a yield of 19 per cent.

[1] S. P. Mulliken, "The Identification of Pure Organic Compounds."

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of the theoretical based upon the ratio $CrO_3 : I_2$. The residue in the distilling flask contained 82.61 per cent. of the original quantity of chromic anhydride.

The quantitative results of the preceding interactions indicate that acetyl chloride is far more reactive with chromic acid than is acetyl bromide, and in turn the acetyl bromide is more reactive than acetyl iodide.

Interaction of Chromic and Acetic Anhydrides.—It has been noted that the solid residues obtained in the preceding reactions were soluble in water, the resulting solutions giving reactions for high concentrations of chromium and acetate ions. The presence of chromic acetate is accordingly inferred. Its formation may be explained thus: Since the interaction between chromic anhydride and the acetyl halide may produce acetic anhydride according to the equation

$$CrO_3 + 2CH_3COX = CrO_2X_2 + (CH_3CO)_2O,$$

and since chromic anhydride does not react with glacial acetic acid, it is possible that chromium acetate owes its formation to a secondary interaction between chromic anhydride and acetic anhydride as produced in the above equation. Chromic anhydride is soluble in acetic anhydride without decomposition, but if the resulting red solution is heated to boiling, a violent reaction ensues, the solution becomes green, and cooling is necessary. The addition of carbon tetrachloride causes the precipitation of a finely divided, light green powder. After filtration and washing with carbon tetrachloride the substance was dried at 100°, and upon analysis was found to contain 22.96 per cent. of chromium, the theoretical for anhydrous chromium acetate being 22.73 per cent.

According to the above method a given amount of chromic anhydride can be converted quantitatively to the acetate. For example, 1.6282 grams of chromic anhydride gave 3.7546 grams of anhydrous chromium acetate, the calculated yield being 3.7313 grams. Anhydrous chromium acetate is slightly deliquescent, soluble in water, alcohol, and hot acetic anhydride.

Interaction of Chromyl Chloride and Silver Acetate.—The failure to obtain a satisfactory yield of chromyl chloride through the interaction of potassium chromate and acetyl chloride was attributed to a secondary reaction between chromyl chloride and potassium acetate yielding chromyl acetate and potassium chloride. The production of the new compound, chromyl acetate or acetyl chromate, may be accomplished through the similar interaction of chromyl chloride and silver acetate, presumably according to the equation

$$CrO_2Cl_2 + 2AgC_2H_3O_2 \longrightarrow (C_2H_3O_2)_2CrO_2 + 2AgCl.$$

When a solution of chromyl chloride in carbon tetrachloride is added to powdered silver acetate, suspended in carbon tetrachloride, the red

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color of chromyl chloride immediately vanishes and a brown precipitate is formed. The end point of the reaction is conveniently determined by the permanency of the red color of chromyl chloride upon the addition of an excess of that reagent. The brown precipitate, after being filtered, washed with carbon tetrachloride, and dried in a vacuum desiccator, was found to be an intimate mixture of silver chloride and a brown, lustrous powder, presumably chromyl acetate. An analysis of this mixture for the content of silver chloride and of chromic anhydride, the latter being calculated as chromyl acetate, gave the following results which substantiate the formation of chromyl acetate:

	Per cent.
Silver chloride	68.79
Chromyl acetate	31.08
Total	99.87

Chromyl acetate is a deliquescent substance and is readily hydrolyzed by water, yielding chromic and acetic acids. A suitable solvent for effecting its complete separation from silver chloride has not yet been found.

A further investigation of the properties of chromyl bromide and of chromyl acetate, and an extension of the reactions herein noted to the preparation of other chromyl compounds, is in progress.

THE PREPARATION OF AMMONIUM SELENATE: A NEW METHOD.[1]

By Frank C. Mathers and Roy S. Bonsib.

Received March 1, 1911.

Introductory Statement.

The object of this research was to determin the best conditions for the preparation of ammonium selenate by the treatment of either barium selenate or lead selenate with an excess of ammonium carbonate. This reaction forms insoluble barium carbonate or lead carbonate, with the ammonium selenate and the excess of ammonium carbonate in solution. This mixture is filtered and the filtrate is evaporated. During the heating, the excess of ammonium carbonate volatilizes and any barium or lead selenate which is in solution is precipitated. This precipitate is filtered off and the pure ammonium selenate allowed to crystallize.

The only method described[2] for the preparation of ammonium selenate is the saturation of selenic acid with ammonia. This method is undesirable because pure selenic acid, itself, is difficult to prepare.

In a method[3] similar to the one described in this paper, barium selenate

[1] From a thesis to be submitted to the Faculty of Indiana University, for the degree of Master of Arts, by Roy S. Bonsib, 1911.

[2] Gmelin-Kraut, *Handbuch*, I, 785 (1907).

[3] Gerichten, *Ann.*, 168, 214.

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is treated with a slight excess of a solution of potassium carbonate. The filtrate from this mixture contains potassium selenate and the excess of potassium carbonate. The disadvantage of this process is that there is no good way of eliminating the excess of potassium carbonate. Potassium selenate cannot be used for the preparation of other selenates by double decomposition. Ammonium selenate is an excellent starting material for making the other selenates by double decomposition.

Barium and lead selenates were selected as starting materials on account of the ease with which they may be obtained in a pure condition. Pure selenic acid, which is difficult to make, is not required for the preparation of pure barium or lead selenate. Selenic acid containing the by-products of its formation may be used. Barium selenate and lead selenate are almost insoluble so they may be obtained by precipitation of any solution containing the SeO_4 ion with barium or lead nitrate. The barium or lead selenate thus formed may be purified easily by washing with water.

Experimental Manipulation.

Extraction of Metallic Selenium.—The selenium was extracted by the potassium cyanide method[1] from flue dust from the roasting of anode slimes from copper refining.

Preparation of Selenic Acid.—A nitric acid solution of selenium dioxide was oxidized to selenic acid with an excess of potassium permanganate. The precipitate of manganese dioxide was removed by filtration. The excess of potassium permanganate in the filtrate, as shown by the pink color, was decomposed with hydrogen peroxide.

Preparation of Barium Selenate.—Barium nitrate solution was added to the hot solution of selenic acid, prepared as described above. The precipitate of barium selenate was filtered and washed. For additional purification, this barium selenate was changed to barium carbonate and ammonium selenate by digestion with ammonium carbonate. The ammonium selenate solution, after separation from the barium carbonate by filtration, was evaporated to crystallization. Pure barium selenate was prepared by precipitating a solution of these crystals with barium nitrate.

Preparation of Lead Selenate.—Lead selenate was prepared in a manner similar to the method for making barium selenate. Lead selenate is more easily filtered and washed than the barium selenate.

Ammonium Carbonate.—Merck's "Ammonium Carbonate" was used. Its composition was: NH_3, 21.8, 21.4; CO_2, 27.7, 27.9 per cent.

Procedure.—Gram portions of barium or lead selenate were weighed out into small beakers and treated with varying quantities of distilled water and pulverized ammonium carbonate. After varying periods of

[1] Nilson, *Ber.*, 7, 1719.

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time, the mixtures were filtered and the residues washed with distilled water, until free from ammonium carbonate, and then analyzed to determin the yield.

Method of Calculating Yields.—The following is the equation for the reaction that takes place, M being either barium or lead:

$$MSeO_4 + (NH_4)_2CO_3 = MCO_3 + (NH_4)_2SeO_4.$$

The residue of either barium or lead carbonate, after filtering and washing free from the ammonium selenate and the excess of ammonium carbonate, was titrated with standard hydrochloric acid and sodium hydroxide. The barium or lead carbonate determined in this way was a measure of the ammonium selenate that was produced. The standard method for the determination of selenium, *i. e.*, precipitating the metallic selenium with sulfur dioxide, filtering, drying and weighing, was used in a few of the experiments as a check to show that the new method of calculating the yields was introducing no error. The titration method gave higher results in all cases, the difference being about 0.5 per cent.

Experimental Data.

Results with Barium Selenate.—Assuming the reaction

$$BaSeO_4 + (NH_4)_2CO_3 = BaCO_3 + (NH_4)_2SeO_4,$$

one gram of barim selenate is equivalent to 0.34 gram of ammonium carbonate. The analysis of the ammonium carbonate that was used in this work showed that it contained only 60 per cent. as much carbon dioxide as is contained in a compound of the composition $(NH_4)_2CO_3$. This analysis was not made until near the close of the work, which accounts for the fractional molecular parts of ammonium carbonate used in the tables.

In the following tables, 0.7 gram of ammonium carbonate represents 1.24 molecules of carbon dioxide to one molecule of barium selenate; 1.48 grams of ammonium carbonate represent 2.48 molecules of carbon

Ammonium carbonate. Grams.	Barium selenate. Grams.	Time treated. Hours.	Water used. cc.	Yield of ammon. selenate. Per cent.
0.7	1	15	5	46.87
0.7	1	29	5	53.38
0.7	1	35	5	55.99
1.4	1	18	10	75.52
1.4	1	24	10	87.23
1.4	1	39	10	91.14
2.8	1	4	10	40.36
2.8	1	8	10	62.50
2.8	1	12	10	74.21
2.8	1	24	10	87.23
2.8	1	28	10	96.35
2.8	1	36	10	97.65
2.8	**1**	**61**	**10**	**97.65**

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dioxide to one molecule of barium selenate; and 2.8 grams of ammonium carbonate represent 4.6 molecules of carbon dioxide to one molecule of barium selenate.

This table shows that a large excess of ammonium carbonate is required. An almost theoretical yield is obtained with five equivalents of ammonium carbonate to one of barium selenate. Ammonium carbonate in excess of 2.8 grams will not dissolve in the amount of water used. The above table also shows that the reaction takes place very slowly, about thirty hours being required to obtain an approximately theoretical yield.

In the following table, one gram portions of barium selenate were treated with 2.8 gram portions of ammonium carbonate.

Time. Hours.	Water used. cc.	Yield of ammon selenate. Per cent.
17	15	72.91
17	20	63.80
17	25	57.29
17	30	49.48
28	15	83.33
28	20	82.03
28	25	72.91
28	30	60.01

This table shows that concentrated solutions give better yields.

Results with Lead Selenate.—Assuming the reaction

$$PbSeO_4 + (NH_4)_2CO_3 = PbCO_3 + (NH_4)_2SeO_4,$$

one gram of lead selenate is equivalent to 0.274 gram of ammonium carbonate. In the following tables, 0.274 gram of the ammonium carbonate that was used in this work represents 0.6 molecule of carbon dioxide to one molecule of lead selenate; 0.55 gram of ammonium carbonate represents 1.2 molecules of carbon dioxide to one molecule of lead selenate; and 1.1 grams of ammonium carbonate represent 2.4 molecules of carbon dioxide to one molecule of lead selenate, one gram of lead selenate being used in each case.

The following table shows that it is necessary to use 1.2 molecules of ammonium carbonate to one molecule of lead selenate, and that the reaction takes place comparatively rapidly. The change of dilution from five cc. to ten cc. is apparently of no effect as long as there is an excess of ammonium carbonate.

Experiments that are not given here show that stirring with air or continuous shaking is of no advantage.

The yields of ammonium selenate were almost theoretical. It is impossible to obtain a yield of 100 per cent. because a small amount of the lead carbonate dissolves[1] in the ammonium carbonate solution and in the wash water. When the solution of ammonium selenate and the wash

[1] Olsen, "Quantitative Chemical Analysis," p. 123 (1905).

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Ammon. carb. Grams.	Water used. cc.	Time. Hours.	Yield of ammon selenate. Per cent.
0.274	10	0.5	47.2
0.274	10	1	48.7
0.274	10	2	50.4
0.274	10	4	53.7
0.274	10	6	55.3
0.274	10	18	56.8
0.274	10	12	56.8
0.274	10	24	58.6
0.55	5	0.5	94.3
0.55	5	1	94.3
0.55	5	3	98.4
0.55	5	16	97.6
0.55	5	22	99.2
0.55	5	28	97.6
0.55	5	30	97.6
1.1	10	0.5	96.0
1.1	10	1	96.0
1.1	10	4	96.0
1.1	10	0.25	96.0
1.1	5	1	93.5
1.1	5	2	96.0
1.1	5	6	96.0
1.1	5	24	96.0

water from the lead carbonate residue are evaporated to drive off the excess of ammonium carbonate and to crystallize the ammonium selenate, the lead selenate is precipitated. This is, of course, filtered out to prevent contamination of the ammonium selenate. In one experiment the weight of this lead selenate was found to be 0.0172 gram; adding this to the yield of ammonium selenate obtained, gives a total of 99.47 per cent., which accounts for practically all of the lead selenate.

Summary.

The best conditions for the preparation of ammonium selenate by the treatment of barium selenate with ammonium carbonate were found to be:

1. 2.8 grams of ammonium carbonate (27.8 per cent. CO_2) to one gram of barium selenate, which is about five molecules of actual ammonium carbonate to one molecule of barium selenate.
2. 10 cc. of water to each gram of barium selenate.
3. The mixture should stand about thirty hours, with occasional shaking.

The best conditions, when using lead selenate with ammonium carbonate, were found to be:

1. 0.55 gram of the ammonium carbonate to one gram of lead selenate which is about 1.2 molecules of actual ammonium carbonate to one molecule of lead selenate.
2. Five cc. of water to each gram of lead selenate.

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3. The mixture should stand about one or two hours to give the best yields, although good yields may be obtained in fifteen to thirty minutes.

The results of these experiments show that lead selenate is the better material to use because it gives a better yield and requires less ammonium carbonate and less time than does the barium selenate.

Increase of temperature, stirring with a current of air or carbon dioxide, or carrying out the reaction in sealed tubes does not increase the yield.

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[CONTRIBUTION OF THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.]

A MODIFICATION OF THE DIPHENYLAMINE TEST FOR NITROUS AND NITRIC ACIDS.

BY W. A. WITHERS AND B. J. RAY

Received February 28, 1911.

Diphenylamine was discovered by Hofmann[1] in 1864, and the blue coloration which he found that it gives with various oxidizing agents has since been used for the detection of the presence of minute amounts of nitric acid.

In 1872 Kopp[2] first proposed its use for the detection of nitrous acid in commercial sulfuric acid.

In 1875 Böttger[3] proposed that the reaction of Kopp be used for the detection of the presence of nitrites and nitrates in potable waters.

Since that time various chemists have given consideration to the subject and have proposed modifications of the methods of applying the test—some of them being very delicate and others less so. It was the need of a reliable and delicate test for nitrites and nitrates which led us to take up this work.

For preparing the reagent Cohn[4] and Wiley[5] use diphenylamine and concentrated sulfuric acid and specify no relation between the amounts except that Wiley refers to 4 cc. of sulfuric acid. Fresenius[6] and Eggermainz[7] use 10 mg. and Muller[8] 20 mg. of diphenylamine to 100 cc. of concentrated sulfuric acid. Warrington[9] dissolves in an indefinit amount of water and adds an indefinit amount of concentrated sulfuric acid. Lunge[10] and Treadwell[11] use 500 mg. of diphenylamine for each 100 cc. of concentrated sulfuric acid and add 20 cc. of water. Hager[12] uses 1 gram to each 150 cc. of acid, and adds 30 cc. of alcohol, and Cimmino[13] uses 5 per cent. of hydrochloric acid without giving the relation between the diphenylamine and sulfuric acid.

The manner of making the test differs with different chemists. To 1 cc. of the liquid to be tested, the amount of diphenylamine reagent to be used is specified as "1 drop," "3 to 4 drops," "a few drops" and "5 cc.," and in some instances no amounts are stated. Some use also sul-

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furic acid in making the test. Some float the liquid to be tested upon the reagent, some mix the liquid and reagent and float the mixture over concentrated sulfuric acid, and Wiley[5] heats at 80 degrees for 15 minutes. Some simply say "treat" and give no details. The table given below shows these facts more in detail.

The manner of making the test is of considerable importance. When the amount of nitrate or nitrite is small it is possible to place the two liquids in layers without the development of a color. In this case the color will develop promptly upon gentle agitation which causes a slight mixing of the liquids at the plane of contact. This blue band may be made to disappear entirely upon thoroughly mixing the liquids if the nitrates and nitrites are in small amounts.

An excess of diphenylamine over the amount required for the reaction actually retards or prevents the development of the coloration. This was shown by us in a series of tests in which varying amounts of the diphenylamine reagent were used. When we used one, two or three drops of the Treadwell[11] reagent, 2 cc. of the liquid to be tested and 2 cc. of concentrated sulfuric acid we obtained a good ring, but when we used five, seven or ten drops of the same reagent and other conditions as before no satisfactory coloration was developed.

The amount of sulfuric acid is extremely important and the addition to it of small amounts of a mixture of diphenylamine reagent and nitrate-bearing liquid which have not given the test will frequently develop a strong coloration.

Warrington in 1885 referred to the greater delicacy of the test in the presence of chlorides and in 1889 Cimmino proposed the use of 5 per cent. hydrochloric acid either by adding a few drops of this acid in making the test or by adding this acid to the solution of the base in sulfuric acid. In a test tube he placed 1 cc. of the solution to be tested, 3 or 4 drops of the diphenylamine solution in sulfuric and hydrochloric acids, 2 cc. of concentrated sulfuric acid and shook. In any case the color develops gradually and reaches the maximum after some minutes; an elevated temperature hastens the development of the color. Practically any of the methods will show the presence of one part of nitrate nitrogen in 10 million.

Combining some of the features of the different methods we have prepared a reagent which in our hands has proven to be very delicate. It is made in the following manner: 700 mg. of diphenylamine are dissolved in a mixture of 60 cc. of concentrated sulfuric acid and 28.8 cc. of distilled water. The resulting mixture is thoroughly cooled and 11.3 cc. of concentrated hydrochloric acid (sp. gr. 1.19) are added slowly, making the hydrochloric acid content 5 per cent. After standing over night some of the base separates, showing that the reagent is saturated. The

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Chemist.	Reagent. Diphenylamine.	H_2SO_4.	H_2O	Other substances	Amount of reagent used.	Amount of unknown used.	H_2SO_4 used.	Temperature.	Time.	Procedure.	Delicacy claimed. 1 part of nitrogen to
Treadwell[11]	500 mg.	100 cc.	20 cc.	..	..	..	..	..	..	Float liquid to be tested on the reagent:	
Cohn[4]	..	..	..	..	few drops	1 cc.	1 cc.	..	..	Mix liquid and reagents, float on H_2SO_4.	13,000,000
Wiley[5]	..	4 cc.	..	..	1 drop	1 cc.	..	80° C.	15 min.	Add 1 drop of reagent to liquid. Keep at 80° for 15 min.	
Frescnius[6]	1 mg.	10 cc.	..	..	few drops	..	..	..	..	Float reagent and liquid over H_2SO_4.	
Hager[12]	1 gram	150 cc.	..	30 cc. alcohol	..	..	..	..	..	Float liquid on reagent.	20,000
Warrington[9]	..	..	..	..	2 drops	2 cc.	5 cc.	..	..	"Treat."	10,000,000
Muller[8]	200 mg.	1 liter	..	..	5 cc.	1 cc.	..	..	..	Treat 5 cc. of reagent with 1 cc. of unknown.	7,700,000
Eggermainz[7]	0.01 gram	100 cc.	..	..	10 cc.	Several cc.	..	..	20 min.	"Treat"	44,200,000
Cimmino[13]	..	..	..	5% HCl	3–4 drops	1 cc.	2 cc.	..	..	Treat and shake.	1,000,000
Withers and Ray	700 mg.	60 cc.	28.8 cc.	11.3 cc. HCl (1.19)	1 drop	1 cc.	2 cc.	40° C.	15 min.	Float liquid and reagent over H_2SO_4, agitate gently. Place in bath at 40° C. for 15 min.	35,000,000
Withers and Ray	700 mg.	60 cc.	28.8 cc.	11.3 cc. HCl (1.19)	1 drop	1 cc.	2 cc.	40° C.	1 hour	Float liquid and reagent over H_2SO_4, agitate gently. Place in bath at 40° for 1 hour.	44,200,000

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test with the diphenylamine reagent as prepared by us is conducted as follows: Place 1 cc. of the liquid to be tested in a clean test tube; add 1 drop of the diphenylamine reagent and mix thoroughly by shaking. From a pipe is added 2 cc. of concentrated sulfuric acid, while the tube is held at an angle so as to form two layers of the liquids. The tube is gently agitated so as to cause a slight mixing of the liquids at the plane of contact, and it is then placed in a bath at the temperature of 40° and left for 15 or 20 minutes. This method will reveal the presence of one part of nitrite nitrogen in 25 million or one part of nitrate nitrogen in 35 million. By heating for one hour instead of 15 or 20 minutes the test will show one part of nitrite nitrogen in 32 million or one part of nitrate nitrogen in 44 million.

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[4] "Indicators and Test Papers," 1907, p. 68.
[5] "Principles and Practice of Agricultural Analysis," I, p. 532.
[6] "Qual. Anal"., Trans., 1906, p. 388.
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[8] *Bull. soc. chim.*, 1889, 670.
[9] *Chem. News*, 51, 41.
[10] *Z. angew. Chem.*, 1894, 345.
[11] Treadwell-Hall, "Analytical Chemistry," 1907, I, p. 340.
[12] *J. Chem. Soc. Abs.*, 50, 99 (1886).
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WEST RALEIGH. N. C.

PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS CONTAINING AMMONIA AND CITRIC ACID.

BY ROBERT A. HALL AND JAMES M. BELL.

Received February 22, 1911.

In the analysis of commercial fertilizers for the so-called "available" phosphoric acid, it is usual to employ a solution of "exactly neutral" ammonium citrate,[1] having a specific gravity of 1.09 at 20°. After extraction of the fertilizer with water, the residue is treated with the citrate solution and the phosphoric acid which remains undissolved is termed insoluble, or non-available; that which the water dissolves is the water-soluble; and that dissolved in the citrate solution is the reverted or citrate-soluble. The sum of the water-soluble and the citrate-soluble phosphoric acid constitutes the available. Upon the results of these analyses depend the valuation of the fertilizer material, and, if the guarantee accompanying the fertilizer claims a higher percentage of phosphoric acid than is shown in the analysis by the state chemist, the manufacturer is liable to a fine.

[1] Bureau of Chemistry, *Bull.* 107 (revised), 1.

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In the preparation of the "exactly neutral" ammonium citrate solution, however, great difficulty is encountered, due to the lack of sensitiveness of every color indicator. This lack of sensitiveness in the color indicator is general in the neutralization of a weak base, such as ammonium hydroxide, by a weak acid, such as citric acid.

The Association of Official Agricultural Chemists prescribes[1] the use of a saturated alcoholic solution of corallin as indicator in testing for the neutrality of the citrate solution; also an "optional method" wherein the citrate is precipitated by an alcoholic solution of calcium chloride, and the filtrate tested for acidity or alkalinity with cochineal as indicator. This method is employed apparently with the object of avoiding the difficulty experienced in determining the end point in the former method. That both methods are unreliable and unsatisfactory is evidenced by the fact that at almost every meeting of chemists engaged in fertilizer analyses there is animated discussion of, and general protest against, both the "official method" and the "optional method" on account of the difficulty in getting a sharp end point with corallin, or any other color indicator.

In the absence of any satisfactory color indicator of the end point in the neutralization of a weak acid by a weak base, several physical properties of mixtures of ammonia and citric acid have been investigated with a view of applying these to the determination of the end point. The use of conductivity as an indicator of neutrality has been demonstrated by Küster and Grüters[2] in the titration of weak acids by strong bases, the conductivity being measured after each addition of the base to the solution. By plotting the quantity of alkali against the conductivity, a decided break was found in the curve just at the neutral point. The solution consisted of a mixture of the acid and salt in varying proportions up to the neutral point, after which it was composed of the alkali and salt. The method of conductance has also been employed to determin the acidity of colored liquids,[3] such as wines, where the color of the liquid would mask the color change of the indicator.

Another physical measurement has been used by Ostwald, *viz.*, density, as an indicator of the neutral point, a sharp break in the composition-density curve being found at this point of neutrality.

The present paper contains the results of measurements of conductivity and of density of a series of solutions containing constant amounts of citric acid and varying amounts of ammonia in a fixed volume of solution. The conductivity measurements were made with the usual Wheatstone apparatus, the conductivity cell used being of the H. C. Jones type, designed for concentrated solutions. In making up the solutions, standardized

[1] Bur. of Chem., *Bull.* 107 (revised), 1.

[2] *Z. anorg. Chem.*, 35, 454 (1903).

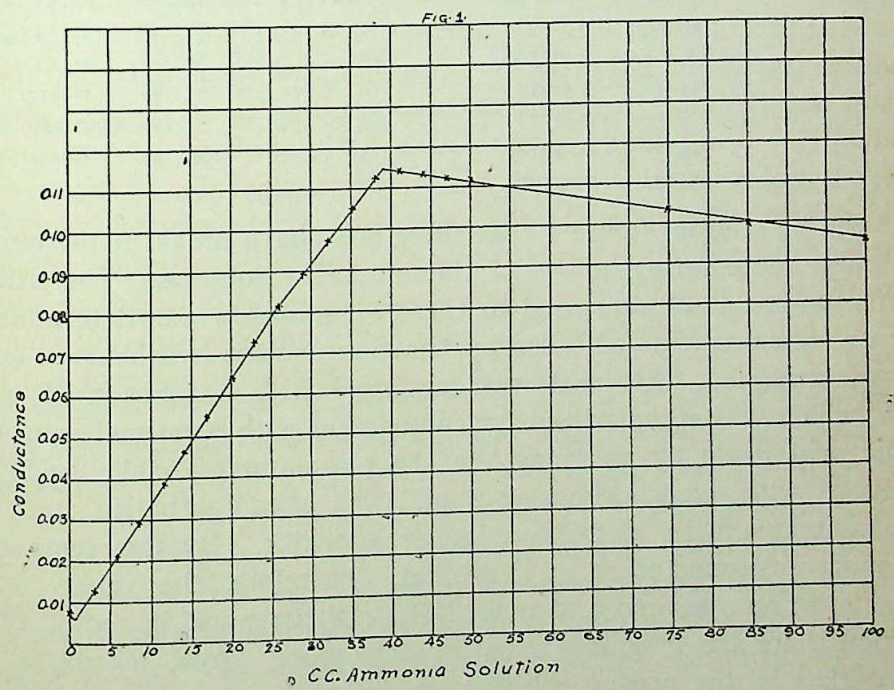
[3] Küster and Grüters, *Loc. cit.*; Geibel, *Z. anorg. Chem.*, 42, 231 (1905).

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(D. & R.) pipets, burets, and flasks were used, and also, as a check, the flask and contents were weighed after each addition. This was deemed advizable on account of the very concentrated solutions used and on account of the volatility of the ammonia. In order to minimize the loss of ammonia by evaporation, the stock solution was siphoned from a bottle protected with a capillary opening. The flow of liquid into the buret was controlled by a glass stopcock, and the top of the buret was closed except for a capillary opening. The outflow from the buret was made through a small tube, drawn to a capillary opening, of sufficient length to pass nearly to the bottom of the flask in which the solutions were mixed. This capillary tube was coated on the outside with a high-melting paraffin to prevent the solution in the flask clinging to the tube when the ammonia solution was led into the body of the citric acid solution. The escape of ammonia was thus minimized or prevented entirely, no ammonia being noticeable by odor or by a change of color of moist neutral litmus paper.

Each solution in the first series of conductivity measurements had a total volume of 200 cc. This contained 100 cc. of a solution of pure citric acid (Kahlbaum's), 370 grams per liter, thus approximating the citrate content of the solution employed in fertilizer analysis.[1] To these solutions were added in the way described above varying amounts of the



ammonia solution, whose exact strength was determined both by titration against standardized acid and also by density determinations. The 200 cc. measuring flask was then cooled and filled up to the mark with dis-

[1] *Loc. cit.*

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tilled water. After thorough mixing, the solutions were transferred to glass-stoppered bottles and placed in the thermostat which was electrically heated and controlled. The temperature was maintained at 25°, within 0.01°. This temperature was chosen rather than 20°, at which the fertilizer chemist makes this specific gravity determination, because of the inconveniences of running a thermostat at a temperature below that frequently existing in this neighborhood.

In another series of measurements the above solutions were diluted one-half, 100 cc. to 200 cc., and the conductivities ascertained.

In Table I are given the results of the conductivity measurements of the concentrated solutions, made as described above. The quantity of citric acid solution used was always 100 cc., weighing 113.00 ± 0.02 grams. In Figure I the conductivities are plotted against the cc. of ammonia.

TABLE I.

Solution no.	Ammonia solution. cc.	Conductivity.	Solution no.	Ammonia solution. cc.	Conductivity.
1.....	0.00	0.007791	12.....	32.00	0.09731
2.....	3.00	0.01292	13.....	35.00	0.1052
3.....	5.75	0.02113	14.....	38.00	0.1124
4.....	8.60	0.02943	15.....	41.00	0.1145
5.....	11.55	0.03901	16.....	44.00	0.1132
6.....	14.31	0.04629	17.....	47.00	0.1124
7.....	17.15	0.05500	18.....	50.00	0.1116
8.....	20.00	0.06401	19.....	75.00	0.1032
9.....	23.00	0.07271	20.....	85.00	0.09990
10.....	26.00	0.08187	21.....	100.00	0.09523
11.....	29.00	0.08984			

It will be seen in Figure 1 that there is a sharp break in the curve at the point representing 39 cc. of the ammonia solution. The strength of the ammonia solution used in these experiments was determined by density measurements and also by titration against hydrochloric acid of known strength. This acid was compared with a solution of caustic soda, which was standardized by comparison with a normal solution of oxalic acid made by weighing the exact amount of oxalic acid. The titrations with oxalic acid were made with phenolphthalein, and those with ammonia with methyl orange as indicator. By this method the ammonia was found to be 13.51 normal. Therefore, the 39 cc. of ammonia solution contain 0.5268 mols. NH_3. Of citric acid in 100 cc. of acid solution there are 37 grams, equal to 0.156 mols. Now, 0.5268/0.176 = 2.993; that is, the neutral solution, as determined by this method is at triammonium citrate.[1] This suggests the applicability of the conductivity method for determining the neutral point of ammonium citrate solution.

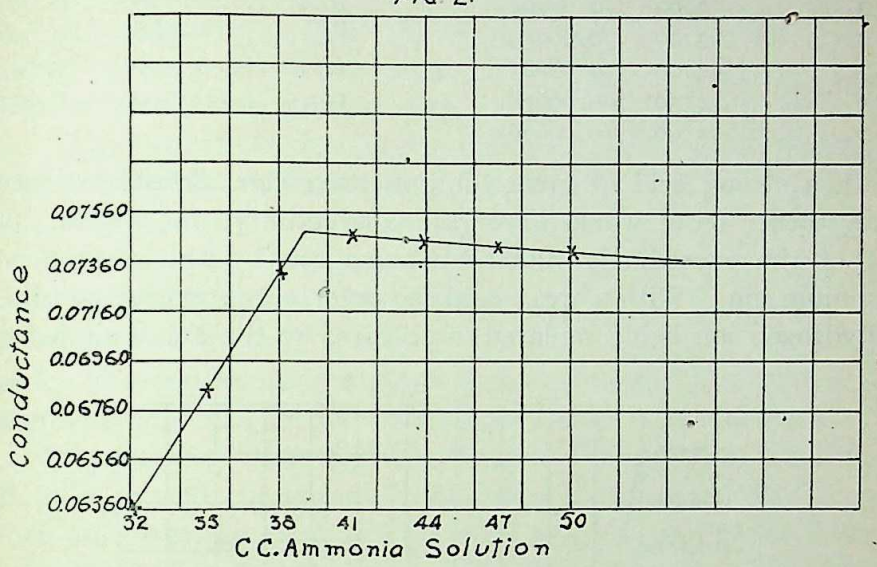
[1] Van Itallie, *Z. anorg. Chem.*, 60, 358 (1908).

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Some of the above solutions were diluted one-half; that is, 100 cc. of the solution were diluted to 200 cc., and the conductivities ascertained. In Table II the measurements are given, and in Fig. 2 the conductivi-

Fig. 2.



ties are plotted against the cc. of ammonia solution as before. The break in the conductivity curve of the diluted solutions agrees with that found for the more concentrated ones, showing that a dilution of one-half has no influence on the neutral point as found by this method.

Table II.

Solution no.	Ammonia solution. cc.	Conductivity.	Solution no.	Ammonia solution. cc.	Conductivity.
12.....	32.00	0.06360	16.....	44.00	0.07440
13.....	35.00	0.06841	17.....	47.00	0.07418
14.....	38.00	0.07330	18.....	50.00	0.07402
15.....	41.00	0.07471			

It will be noticed further in the curve of Fig. 1 that the first point of the curve does not fall in the smooth curve with the other points up to the neutral point. To investigate the failure of this point to fall on the regular curve there was made a further series of measurements in which the quantities of ammonia solution added differed by smaller increments (0.5 cc.). This showed that the curve has a minimum. In a further series of measurements having a still smaller increment of ammonia solution (0.1 or 0.2 cc.) the region of this minimum was more carefully investigated. In this series the original ammonia solution was diluted ten times, and so 0.1 or 0.2 cc. of the original solution correspond to 1 or 2 cc. of the diluted solution. In Table III the measurements are given and in Fig. 3 the conductivities are plotted against the number of cc. of the diluted ammonia solution.

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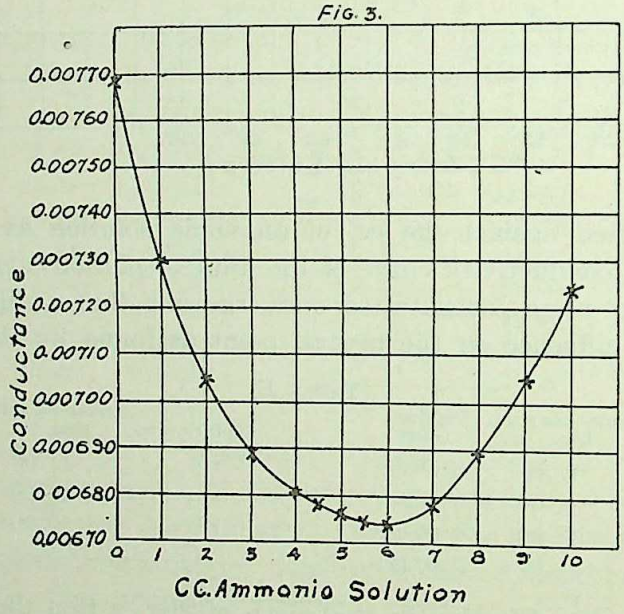
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TABLE III.

Solution no.	Ammonia. cc.	Conductivity.	Solution. no.	Ammonia. cc.	Conductivity.
1.....	0.00	0.00768	8.....	5.50	0.00674
2.....	1.00	0.00730	9.....	6.00	0.00674
3.....	2.00	0.00704	10.....	7.00	0.00678
4.....	3.00	0.00689	11.....	8.00	0.00689
5.....	4.00	0.00681	12.....	9.00	0.00705
6.....	4.50	0.00678	13.....	10.00	0.00724
7.....	5.00	0.00676			

With a strong acid at great dilution successive additions of ammonia (or any other base) would lower the conductivity, due to the displacement of the exceedingly mobil hydrogen ion by the slower moving ammonium ion. With a weak acid, however, two opposing factors enter, the hydrogen ion being replaced, as before, by the ammonium ion, and

FIG. 3.



also the salt having a far higher degree of dissociation than the acid. The second factor is probably the predominant one and slight additions of ammonia would increase the conductivity. Should the citric acid contain a minute amount of a strong acid, the strong acid would be neutralized first, and thus give a minimum conductance. Whether this minimum be due to impurities, or whether other weak bases and weak acids exhibit the same phenomenon is still under investigation in this laboratory.

Another method of determining the neutral point of ammonium citrate solution was suggested by the fact that chloroform dissolves free ammonia[1]

[1] Hantzsch and Sebaldt, *Z. physik. Chem.*, 30, 266 (1899); Abbott and Bray, THIS JOURNAL, 31, 729 (1909).

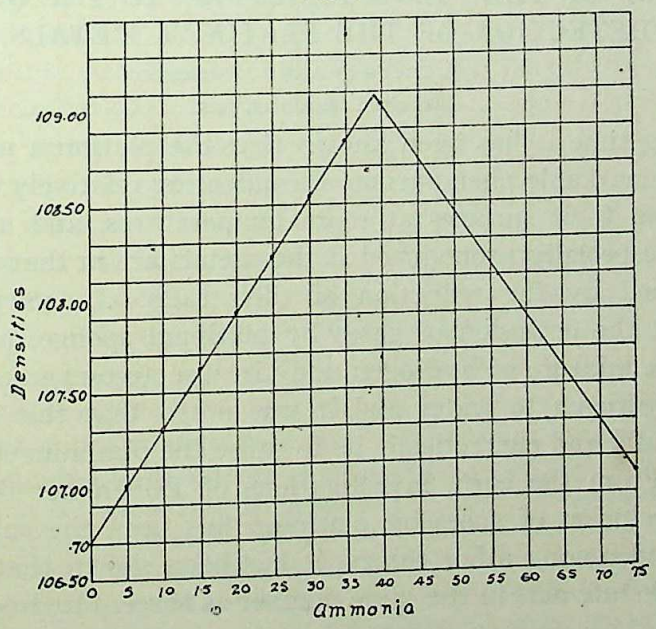
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but does not dissolve citric acid or ammonium citrate and therefore may be used as an agency for removing NH_3 from its salts, if ammonia be present in excess. A series of nine solutions, containing 35, 36, 37 ..... 43 cc. of ammonia solution, respectively, was prepared, and each solution shaken with chloroform. The chloroform extracts from the solutions containing 35 to 39 cc. of ammonia solution showed no free ammonia on titration with dilute sulfuric acid, methyl orange being used as indicator. The extracts from solutions containing 40 to 43 cc. of ammonia solution contained increasing amounts of free ammonia. Thus the presence of free ammonia in the citrate solution may be detected by shaking out with chloroform and testing the chloroform layer for free ammonia. This offers another method for establishing the end point when citric acid is being neutralized by ammonia.

A series of measurements of the densities of solutions containing citric acid and ammonia offer further confirmation of the position of the neutral point. In preparing these solutions 50 cc. of citric acid solution were placed in a 100 cc. measuring flask and ammonia was added. Water was then added to the mark and the flask and contents weighed and the density computed in the usual way. In Table IV the data thus obtained are given, and in Fig. 4, the number of cc. of ammonia solution is

Fig. 4.



plotted against the densities. It is seen that the neutral solution has the maximum density and that this solution is the same as that indicated by the break in the curve obtained by the conductivity method.

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TABLE IV.

Solution no.	Ammonia solution. cc.	Density.	Solution no.	Ammonia solution. cc.	Density.
1.....	0	1.0670	7.....	30	1.0853
2.....	5	1.0700	8.....	35	1.0883
3.....	10	1.0731	9.....	40	1.0903
4.....	15	1.0762	10.....	45	1.0874
5.....	20	1.0792	11.....	50	1.0846
6.....	25	1.0822	12.....	75	1.0702

Summary.

In this paper it has been shown that the neutral point for a weak acid and a weak base, such as citric acid and ammonia, may be accurately determined by conductivity measurements; that the presence of an excess of ammonia in the ammonium citrate solution may be ascertained by shaking out with an immiscible solvent, as chloroform, which dissolves a part of the excess of the base but neither the free acid nor the salt; and that the neutral point of the ammonium citrate solution may also be established by density determinations.

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CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY OF THE COLLEGE OF THE CITY OF NEW YORK.]

APPLICATION OF THE "GLOW REACTION" TO THE QUALITATIVE DETECTION OF THE PLATINUM METALS.[1]

BY L. J. CURTMAN AND P. ROTHBERG.

Received March 15, 1911.

For a long time it has been known that the platinum metals present the rather remarkable phenomenon of condensing relatively large volumes of gases upon their surfaces at room temperatures, and also, that this property is especially pronounced if the metals are in that finely divided state obtained by the reduction of their salts. In 1823 Döbereiner[2] showed that the occlusion of gases by platinum sponge, particularly in the case of a mixture of hydrogen and air, was accompanied by the oxidation of hydrogen to water and it was noted that this reaction took place so rapidly and energetically as to cause the platinum sponge to glow intensely. From the early investigations of Döbereiner to the present day, this occlusion of gases by platinum has been the subject of much research,[3] and among other things, it has been shown that hydrogen in the occluded state acts in the same manner as nascent hydrogen[4] and that,

[1] Presented at the March meeting of the New York Section of the American Chemical Society.

[2] Schweigger, *J. für. Chem.*, 39, 159 (1823).

[3] J. L. Howe, "Bibliography of the Platinum Metals" in *Smithsonian Inst. Misc. Collections*, Vol. 38.

[4] T. Graham, *Proc. Roy. Soc.*, 16, 422 (1868).

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in general, the presence of metallic platinum in the finely divided state greatly accelerates the oxidation of many oxidizable gases.[1]

Although this property of platinum has been made use of in the analysis of gases and in various commercial processes, the authors are not aware of any record which shows that the occlusion of gases and their oxidation in the presence of the platinum metals, more particularly the glow accompanying the oxidation of some gases, has been utilized as a method for the detection of platinum and its allied metals. It was the object of this investigation to determin the reliability for qualitative purposes of the "glow reaction" obtained by passing a mixture of air and illuminating gas over very finely divided platinum. To that end it was necessary, first, to decide upon a simple method of carrying out the reaction; second, to determin the minimum amount of each of the platinum metals that would give the test; and third, in the case of platinum to ascertain the influence and possible interference of other substances.

Method of Making Tests.—The following method was selected and though it may not be the most delicate or refined method possible, it has decided advantages as a practical method, because of the simple apparatus necessary and the great rapidity with which it may be applied.

The substance to be tested is brought into solution by any of the common methods and about 0.2 cc. of this solution is absorbed in a piece of thin asbestos paper by alternately dipping the paper into the solution and heating until the required volume has been absorbed. Experience showed the above volume (0.2 cc.) to give the best results in these tests. The moist paper held by one end in a pair of tongs is now heated to redness in the Bunsen flame, then removed, and after the redness has ceased, but while the paper is still hot, it is brought into a stream of a mixture of illuminating gas and air from a Bunsen burner. If platinum is present, the asbestos paper will begin to glow.[2] The glow must last for some time and can be brought back after it has once died out by again heating the paper and holding it in the stream of gas.[3] The burner must be arranged.

[1] W. Henry, *Phil. Trans.*, 14, 266 (1824); Phillips, *Am. Chem. J.*, 16, 163.

[2] In the absence of substances which on ignition leave a heavy residue, failure to obtain the glow at this point would show that the metal tested for was not present in the volume absorbed in an amount as great as that indicated below as the limit for that metal. It is obvious that the given solution must be concentrated according to the refinement of the analysis to such an extent that 0.2 cc. will contain sufficient metal to give the test. For example, should it be desired to ascertain whether 0.05 mg. of platinum were present in 500 cc. of a given solution, concentration to such a point would be necessary that 0.2 cc. should contain 0.002 mg. platinum (the limit for that metal). In the above example 20 cc. of the solution must be concentrated to 0.2 cc. If smaller quantities were to be detected, it would be necessary to concentrate a larger amount of the solution.

[3] This cannot be done indefinitly if the quantity of metal is small, owing perhaps to mechanical loss or change of state of the platinum black, as shown by Berthelot, *Compt. rend.*, 94, 1377 (1882).

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to supply a fairly good mixture of illuminating gas and air and the pressure must not be too great.

It is also essential for the greatest sensitiveness of the test that the asbestos paper be very thin. In these experiments pieces of asbestos paper 0.5 × 3.0 cm. and 0.3 mm. thick were employed, only approximately half being used to absorb the liquid. The intensity of the glow can be somewhat increased by having the gas warm. This can be easily accomplished by slightly warming the upright tube of the burner before passing the gas through it. All the results given below, however, have been obtained with the gas at room temperatures.

Determination of the Limits of the Test.—To determin the smallest quantity of each of the platinum metals that would give an unmistakable glow under the conditions of the above method, the following experiments were performed.

Platinum.—For this metal crystals of Merck's chloroplatinic acid were dissolved in water and the yellow solution thus obtained standardized and found to contain 0.00214 g. platinum per cc. Portions of this solution were successively diluted and known volumes of the solutions thus obtained were absorbed in asbestos paper and the test applied. The smallest amount of platinum that gave a reliable glow was that contained in 0.1 cc. of a colorless solution whose strength was 0.02 mg. platinum per cc. The limiting amount for platinum is therefore 0.002 mg. As this quantity of platinum was contained in 0.1 cc., the dilution was one part in fifty thousand.[1]

Palladium.—0.4856 g. Merck's palladium foil were dissolved in aqua regia and repeatedly evaporated to dryness with the addition of hydrochloric acid. The residue was then taken up with 100 cc. of water,

[1] It would seem from the figure for the dilution that the glow test is less sensitive than the potassium iodide test proposed by Field, *Chem. News*, 45, 262 (1882), and now in general use in testing for small quantities of platinum. Field obtained a test for platinum in a dilution of one part in two million by allowing the solution tested to stand for some time after the addition of the potassium iodide. But it is to be noted that the amount of platinum present was 1 mg., a quantity five hundred times as great as that necessary for the glow test. It is obvious that the *small amount* and not the *dilution* is significant in stating the sensitiveness of the glow reaction. For, whatever the initial dilution be, the solution to be tested can by proper concentration give a glow test provided the limiting amount of platinum be present. To compare the two tests several solutions containing the limiting amount of platinum one part in 50,000 were prepared, and Field's test applied to each of them. Extreme care was taken with these tests which were controlled by blanks run under the same conditions, yet no change of color could be observed in the solutions though they were frequently examined for a period of two days. Similar solutions, however, very readily gave excellent glow tests. Again the potassium iodide test requires modification, if Fe (=ic), Ni, Pb, Cu, Hg, Bi, Au and substances yielding darkly colored solutions in general be present, whereas, as shown below, the glow test can for practical purposes be applied to solutions containing all the metals.

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giving a dark brown solution containing 0.004856 g. palladium per cc. Portions of this solution were successively diluted and the test applied in the same manner as for platinum. As small a volume as 0.1 cc. of a colorless solution containing 0.0049 mg. palladium per cc. was found to be the smallest amount that gave a good glow. Thus the limit for palladium under the conditions of the test is 0.0005 mg.

Iridium.—Powdered iridium[1] was converted to sodium hexachloroiridate by intimately mixing the iridium with sodium chloride and heating the mixture in an atmosphere of chlorine. The fused mass thus obtained was dissolved in water, filtered and the reddish brown filtrate obtained used for the iridium tests. This solution was found on analysis to contain 0.004 g. iridium per cc. The limiting quantity of iridium that gave the test was 0.005 mg. This amount was contained in 0.1 cc. of a pale yellow solution formed by diluting one cc. of the original solution to 75 cc. The determinations for iridium were made under rather unfavorable conditions as the salt used contained an excess of alkali, the presence of which, as shown below, is not favorable to the test.

Rhodium.—A dark brown solution of rhodium tetrachloride was standardized and found to contain 0.1156 g. of rhodium per cc. Portions of this solution were repeatedly diluted and known volumes tested. The limit for this metal was found to be 0.0009 mg., which quantity was contained in 0.1 cc. of a colorless solution.

Osmium.—Finely divided metallic osmium was converted to sodium hexachlorosmate by the same method as that employed for the preparation of the corresponding iridium compound. Fairly strong solutions of this salt failed to give a glow. Solutions of sodium osmate, obtained by absorbing in sodium hydroxide the osmium tetroxide vapors which were distilled over in heating metallic osmium with fuming nitric acid, gave similar negative results. The failure to obtain the test with this metal is very likely due to the volatility of the osmium salts under the conditions of the test.

Ruthenium.—With this metal negative results were also obtained, even from fairly strong solutions of K_2RuCl_5, $K_4Ru(CN)_6.3H_2O$, and $K_2RuNOCl_5$.[2]

The cause of these negative results is probably the same as that stated for similar results obtained with osmium.

Having established the method and the limits for the various metals, it was thought desirable to ascertain the possible interference of other substances present in a solution to be tested for platinum. To this end, solutions were made containing chloroplatinic acid and a salt of

[1] Obtained through the kindness of Belais and Cohn, New York, to whom we wish to express our thanks.

[2] These salts were obtained through the kindness of Prof. J. L. Howe, of Washington and Lee University, to whom we wish to acknowledge our thanks.

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a foreign metal whose influence it was desired to determin. The amount of platinum present in the volume absorbed in no case deviated much from the average, which was 0.01 mg. In every case a distinct glow was obtained and the following table shows the ratio of the foreign metal to the platinum in the solutions tested.

RATIO OF THE METAL TO PLATINUM, 10,000 TO 1 OR GREATER.

Metal.	Compound used.
Silver	$AgNO_3$
Mercury	$HgNO_3.H_2O$
	$Hg(NO_3)_2.{}^1/_2H_2O$
	HgCl
Bismuth	$Bi(NO_3)_3.5H_2O$
Copper	$CuSO_4.5H_2O$
Cadmium	$Cd(NO_3)_2.3H_2O$
Antimony	$SbCl_3$
Tin	$SnCl_2.2H_2O$
Aluminium	$AlCl_3.6H_2O$

RATIO OF METAL TO PLATINUM, 3,000 TO 1 OR GREATER.

Metal.	Compound used.
Lead	$Pb(C_2H_3O_2)_2.3H_2O$
Chromium	$Cr(NO_3)_3.9H_2O$
Iron	$FeCl_3.6H_2O$
Nickel	$NiCl_2.6H_2O$
Cobalt	$CoCl_2.6H_2O$
Manganese	$MnCl_2.4H_2O$
Zinc	$ZnSO_4.7H_2O$
Barium	$BaCl_2.2H_2O$
Strontium	$SrCl_2.6H_2O$
Calcium	$CaCl_2$
Magnesium	$Mg(NO_3)_2.6H_2O$
Ammonium	NH_4Cl
	Sulfur
	Starch
	Gelatin

RATIO OF METAL TO PLATINUM, 1,000 TO 1 OR GREATER.

Metal.	Compound used.
Beryllium	$BeSO_4.4H_2O$
Lanthanum	$La(NO_3)_3.6H_2O$
Thorium	$Th(NO_3)_4.12H_2O$
Uranium	$UO_2(NO_3)_2.6H_2O$
Cerium	$Ce(NO_3)_3$
Erbium	$Er(NO_3)_3.6H_2O$
Zirconium	$Zr(NO_3)_4.5H_2O$
Yttrium	$Yt(NO_3)_3.4H_2O$
Tungsten	$Na_2WO_4.2H_2O$
Arsenic	As_2O_3
	$Cu_3(AsO_4)_2.4H_2O$
Praseodymium	$Pr(NO_3)_3.6H_2O$
Neodymium	$Nd(NO_3)_3.6H_2O$
Cesium	CsCl
Rubidium	RbCl.

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Comments on Table and Further Experiments on Interfering Substances.—It is to be understood in the interpretation of the above table that the numbers given do not represent the maximum ratios of foreign metal to platinum that might be present in a solution tested for platinum except in the case of lead and arsenic. These metals hindered the test when present in proportions greater than those stated above; but with all the other metals tried, a good test was obtained in the ratios mentioned, and as these were fairly high no attempt was made to determin the maximum quantity of each metal in the presence of which the test would still apply. Uniform ratios, however, were not used because of the different solubilities of the various salts, and because of the comparative rarity of some of them.

Relatively large quantities of the alkalies were found to interfere and experiments made with solutions of Na_2SiO_3, Na_2CO_3, NaOH, $Na_2B_4O_7$, Na_2SO_4, NaCl, $NaKC_4H_4O_6$, NaF, KCl and LiCl showed eight hundred parts of alkali metals to one of platinum to be approximately the greatest ratio of alkali to platinum that would glow under the conditions of the test.[1]

With gold, experiments performed on a solution of auric chloride gave a maximum ratio of 500 parts of gold to one of platinum. On adding a crystal of oxalic acid and precipitating the gold, a test was obtained on a solution containing 2500 parts of gold to one of platinum.

In general it may be said that all substances which, after ignition, leave a heavy residue on the asbestos paper, impair the sensitiveness of the test insofar that quantities of platinum near the limit will not glow under these conditions. Also, solutions which are acid with strong nitric acid attack the asbestos paper, swelling it up and thus also decreasing the sensitiveness of the test. It can, however, be seen from the above results that none of the common metals offers any interference to the glow tests unless present in quantities that are considerably larger than the quantity of platinum.

Furthermore, the test was applied directly without going through any separations, to a sample of "black sand," of California, to platinum residues, sweepings and various forms of platinum waste. In each case a good test was obtained.

Tests made on solutions of palladium containing respectively lead, arsenic, and sodium (the least favorable of the common metals) seem to warrant the belief that palladium will be as little affected by the presence of other metals as was found in the case of platinum.

Summary.

1. The oxidation of the constituents of illuminating gas, particularly of hydrogen, with finely divided platinum, palladium, rhodium, or iridium

[1] Phillips finds a similar interference of alkali in experiments on the oxidation of gases by means of palladiumized asbestos, *Am. Chem. J.*, 16, 168.

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as catalytic agent is accompanied by a glow which is distinctly characteristic of these metals. Hence this glow may be used as a qualitative test for these metals.

2. This test is sensitive to extremely small quantities of the metals, the limits being: platinum, 0.002 mg.; palladium, 0.0005 mg.; rhodium, 0.0009 mg.; and iridium, 0.005 mg.

3. The presence of other substances does not for practical purposes interfere with this test. In fact, the test may be applied directly to a solution without preliminary treatment for the separation of other substances.

4. In an analysis where all the platinum metals are to be considered, this test may serve to show the presence of the platinum group with the exception of osmium and ruthenium, and also to confirm the presence of platinum, palladium, rhodium and iridium, when the metals have been separated. In most practical work, the "glow reaction" becomes distinctly a test for platinum, the most common metal of the group. For this latter purpose the glow test recommends itself strongly, because of its sensitiveness and the rapidity with which it gives results.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY OF THE COLLEGE OF THE CITY OF NEW YORK.]

A STUDY OF THE FACTORS INFLUENCING THE SYSTEMATIC QUALITATIVE DETERMINATION OF BARIUM.[1]

BY LOUIS J. CURTMAN AND EDWARD FRANKEL.

Received March 15, 1911.

Experience with qualitative unknowns has shown that by means of a systematic qualitative analysis it is almost impossible to detect as much as 25 and in many cases 50 milligrams of barium with the group reagent $(NH_4)_2CO_3$. The failure to obtain the test at this point is due to losses which are entailed throughout the analysis. These may be accounted for under the following heads:

1. Influence of the hydrogen sulfide group;
2. Influence of the ammonium sulfide group;
3. Sensitiveness of the group and confirmatory reagent;
4. Influence of the presence of impurities (sulfates) in the various reagents employed.

1. *Hydrogen Sulfide Group.*—To determin the losses involved in the precipitation and removal of the metals of the copper group by hydrogen sulfide, a typical metal such as copper was taken. This metal furthermore possesses the advantages that its sulfide offers no difficulty in filtering and

[1] Read at the March meeting of the New York Section of the American Chemical Society.

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washing. The procedure employed to determin whether or not there is a loss involved in this part of the analysis was as follows:

A solution was prepared containing 100 mg. copper as copper nitrate,[1] and a definit quantity of barium as barium chloride accurately delivered from a buret. To this was added 2.5 cc. of hydrochloric acid (sp. gr. 1.2) and the bulk then made up to 100 cc. The solution was then heated over a low flame to about 70° and treated with a rapid stream of hydrogen sulfide until precipitation was complete. The precipitate was allowed to settle and the clear supernatant liquid filtered off. The precipitate was washed three times by decantation with water containing hydrogen sulfide, and finally on the filter until free of chlorides. The filtrate and washings were caught in a 500 cc. Erlenmeyer flask, boiled to expel the hydrogen sulfide[2] and then allowed to stand over night. An examination of the filtrate the next day showed the presence of a white finely divided precipitate which had settled to the bottom of the flask. This was then filtered off on ashless paper and the barium in the clear filtrate determined as barium sulfate. The following results were obtained:

TABLE I.—100 MG. Cu, 2.5 CC. HCl (SP. GR. 1.2) VOL. 100 CC.

Ba taken. Mg.	Ba recovered. Mg.	Ba lost. Mg.
128.7	127.5	1.2
128.7	126.9	1.8
128.7	127.6	1.1
100.0	98.5	1.5
100.0	98.2	1.8
100.0	98.8	1.2
		Average loss, 1.4

The presence of oxidizing agents in the solution subjected to treatment with hydrogen sulfide for the removal of the copper and tin groups will have the effect of oxidizing the hydrogen sulfide with the formation of a little sulfuric acid and a large separation of sulfur. The most common of these substances are nitric acid, permanganates, dichromates and ferric chloride. The first three of these readily reveal their presence and should be eliminated before precipitation with hydrogen sulfide. The presence of ferric chloride in appreciable amounts cannot be detected by inspection, because of the obscuring influence of other colored substances. For this reason and because its removal at this point cannot be conveniently accomplished it is generally left in solution. To determin its effect[3] in the second group precipitation a solution containing 100 mg.

[1] All materials used in this work were tested and found free from sulfates.

[2] A blank run to determin whether this operation involved a mechanical loss gave good results, showing the procedure to be entirely satisfactory.

[3] Noyes and Bray, THIS JOURNAL, 29, 191, call attention to the fact that the presence of 500 mg. of iron as $FeCl_3$ will have the effect of precipitating as much as 20 mg.

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copper as copper nitrate, 100 mg. Fe‴ as ferric chloride, an accurately measured amount of barium as barium chloride and 2.5 cc. hydrochloric acid (1.2) in 100 cc. were warmed to 70° and the copper sulfide precipitated as before. The filtrate and washings from this precipitation were caught in a flask and boiled to expel the hydrogen sulfide. On standing over night a white residue settled out and was filtered off. The clear filtrates were then oxidized by boiling with 1–2 cc. of conc. nitric acid and the iron precipitated with ammonia as ferric hydroxide. The latter was filtered off and washed free of chlorides. The barium in the clear filtrate was then determined as barium sulfate.

In this procedure there are two losses to be considered: (1) The loss due to the reduction of the ferric chloride by hydrogen sulfide; and (2) the loss involved in the precipitation of the ferric hydroxide by ammonia. The latter factor will be discussed under the influences of the precipitation of the third group. The loss due to the oxidizing effect of ferric chloride on the hydrogen sulfide will be represented by the difference between the total loss sustained and those due to influences other than that of ferric chloride.

The results obtained were:

TABLE II.—100 MG. Cu, 100 MG. Fe‴, 2.5 CC. HCl (1.2), VOL. 100 CC.

Ba taken. Mg.	Ba recovered. Mg.	Ba lost. Mg.	Ba lost, due to $Fe(OH)_3$ pptn. See Table IV. (Av). Mg.	Ba lost, due to $FeCl_3$. Mg.
100	70.9	29.1	14.7	14.4
100	72.3	27.7	14.7	13.0
100	72.5	27.5	14.7	12.8
100	69.4	30.6	14.7	15.9
				Average loss, 14.0

If instead of Cu, whose sulfide behaves well, Sn^{iv} or Cd were selected as the second group metal, it might be expected that large losses would be found, because of the well known tendency of the sulfides of these metals to pass through the filter in the colloidal state. With Sn^{iv} this difficulty was surmounted by the use of a double filter,[1] a clear filtrate being readily obtained in one filtration even from a cold solution.

In the case of cadmium sulfide, however, difficulties in filtration were encountered, for even with a double filter the precipitate ran through and a clear filtrate could only be obtained by repeated filtration through the same filter. The precipitate, however, on washing, did not tend to go

of barium as sulfate in the second group precipitation with H_2S. As their procedure, which was somewhat different from ours, was not carried out on a strictly quantitative basis, it was thought desirable to proceed with the above work in order to obtain results which would be comparable with others obtained under parallel conditions.

[1] Schleicher and Schull, No. 595, 12½ cm.

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through in a colloidal condition as is the case with zinc sulfide. After a number of preliminary trials the following procedure was adopted: A solution containing 100 mg. cadmium as cadmium nitrate, a definit amount of barium chloride and 2.5 cc. hydrochloric acid (sp. gr. 1.2) in 100 cc. was prepared. The solution was treated in the cold[1] with a rapid stream of hydrogen sulfide until precipitation was complete. The precipitate was then filtered through a double filter and the filtrate, which was cloudy, refiltered through the same filter, the funnels being covered during filtration to prevent oxidation. After two refiltrations a clear filtrate was obtained. The precipitate was then washed on the filter with a 5 per cent. solution of ammonium nitrate containing hydrogen sulfide. The filtrate and washings were caught in a 500 cc. Erlenmeyer flask, boiled to expel the hydrogen sulfide and allowed to stand over night. Contrary to expectations, no white residue settled out as in the case of copper. The clear liquid was then transferred to a beaker and the barium determined as barium sulfate.

TABLE III.—100 MG. Cd, 2.5 CC. HCl (SP. GR. 1.2), VOL. 100 CC.

Ba taken. Mg.	Ba recovered. Mg.	Ba lost. Mg.
100	100.1	—0.1
100	99.3	+0.7
100	100.0	+0.0
100	100.5	—0.5
100	100.5	—0.5

The results obtained indicate that the losses entailed in this procedure are practically negligible.

Failure to obtain a loss with cadmium would seem to indicate that this was partly due to the fact that the beakers and funnels were covered as much as possible during the process of filtration, which was not the case with the experiments on copper. To test this point, a number of copper determinations were run under the same conditions as before except that care was taken to keep the beakers and funnels covered as much as possible in the course of filtration. The results, however, were substantially the same and the losses no lower than those already recorded. This would seem to indicate that the rate of oxidation of cadmium sulfide is smaller than that of copper.

Work is now being done in this laboratory to determin the relative rates of oxidation of sulfides, the results of which will shortly be published.

2. *The Influence of the Ammonium Sulfide Group.*—The third analytical group was studied in a manner similar to that pursued in the investigation of the second group. Here the three influences deserving prime consideration are:

[1] Noyes and Bray, THIS JOURNAL, 29, 168, state that Cd is completely precipitated by H_2S only in the cold. Some experiments made by us confirm this statement.

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1. Precipitation with NH_4OH.
2. Precipitation with $(NH_4)_2S$.
3. Precipitation and filtration of a colloidal sulfide as zinc sulfide.

Influence of the Precipitation with Ammonium Hydroxide.—It is considered desirable by some chemists in the absence of phosphates,[1] etc., to precipitate the trivalent metals of the third group with ammonia rather than separate them together with the divalent elements of the third group with ammonium sulfide. Such a procedure involves losses of the alkaline earths, due to the absorption of carbon dioxide from the air by the alkaline liquid, resulting in the partial precipitation of the carbonates of the alkaline earths with the metals of this group. To determin exactly the extent of this loss, a solution, containing definit amounts of ferric chloride and barium chloride, was made up to 100 cc., boiled and treated with an excess of ammonium hydroxide and boiled. The precipitated ferric hydroxide was filtered off and washed free of chlorides, the operation taking about 40 minutes. The clear filtrates were then analyzed for barium. Contrary to expectations the loss in this operation was far greater than one might think. The results of a number of determinations made to determin this loss are:

TABLE IV.—100 MG. Fe‴, 2.5 CC. HCl (1.2), VOL. 100 CC.

Ba taken. Mg.	Ba recovered. Mg.	Ba lost. Mg.
100	84.9	15.1
100	85.5	14.5
100	84.5	15.5
100	86.2	13.8
	Average loss,	14.7

Influence of the Precipitation with $(NH_4)_2S$.—In the precipitation of the metals of the ammonium sulfide group losses were expected, resulting from two distinct causes, *viz.*:

1. The absorption of carbon dioxide by the alkaline liquid.
2. The oxidation of the precipitated sulfide.

To minimize the effect of the first cause the solution was kept acid until the moment of precipitation. To determin the loss due to the second cause, the metal cobalt was chosen as a typical metal of this group, because it involves no complications in precipitation and filtration. The combined effect of the precipitation of copper and cobalt was determined in the following manner:

[1] That the presence of phosphates and oxalates may cause the alkaline earth metals to precipitate in the ammonium sulfide group is well known; but as this difficulty is successfully overcome by the use of a modified scheme, it was thought undesirable to consider this factor, particularly in view of the recent work of Noyes, Bray and Spear (THIS JOURNAL, 30, 485, 498, 518), which provides an adequate procedure for the treatment of such cases.

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A solution containing 100 mg. copper as copper nitrate, 100 mg. cobalt as cobalt nitrate, a definit amount of barium chloride and 2.5 cc. hydrochloric acid (1.2) in 100 cc. was prepared. It was warmed to about 70°, and the copper precipitated by hydrogen sulfide. The precipitate was filtered and washed as in the previous case and the filtrate boiled to expel the hydrogen sulfide. On standing over night there invariably settled out of the filtrate a white residue which was filtered off. The clear filtrate was warmed, made alkaline with ammonia and immediately treated with hydrogen sulfide. The precipitated cobalt sulfide was filtered off and washed, first by decantation with water containing ammonium sulfide and then on the filter until free of chlorides. The combined filtrate and washings colored slightly yellow were caught in a Kjeldahl flask, acidified with hydrochloric acid and boiled to expel the hydrogen sulfide. As the bumping in this last operation was very violent, a Kjeldahl flask was used to prevent mechanical loss. The filtrates on acidification contained a large amount of finely divided sulfur which coagulated on boiling. The filtrate was allowed to stand over night, the residue filtered off and the barium in the clear filtrate determined as barium sulfate. The results obtained were:

TABLE V.—100 MG. Cu, 100 MG. Co, 2.5 CC. HCl (1.2), VOL. 100 CC.

Ba taken. Mg.	Ba recovered. Mg.	Ba lost. Mg.	Loss due to CuS pptn.	Loss due to CoS pptn.
100	96.2	3.8	1.4	2.4
100	96.6	3.4	1.4	2.0
100	96.6	3.4	1.4	2.0
100	96.1	3.9	1.4	2.5
				Average loss, 2.2

Colloidal Sulfides.—When nickel sulfide is precipitated by an excess of ammonium sulfide, some nickel sulfide is dissolved by the reagent to form a brown liquid, which passes through into the filtrate. In such a condition the oxidation of nickel sulfide to sulfate is probably rapid and would have the effect of throwing out some barium as barium sulfate. This difficulty may, however, be obviated by precipitating the nickel from a hot ammoniacal solution with hydrogen sulfide. This procedure was used by us successfully with solutions containing varying amounts of ammonia, the concentrated filtrates from the nickel sulfide in no case giving a test for nickel with dimethyl glyoxime, thus confirming the work of Noyes, Bray and Spear[1] on this point.

With zinc a different problem was encountered. Because of the well known tendency of zinc sulfide to pass through even a double filter, there is much trouble in obtaining a clear filtrate from the third group, if zinc is present. The presence of other sulfides tends to prevent the zinc sul-

[1] THIS JOURNAL, 30, 536, 1908.

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fides from passing through the filter, but when zinc is present alone, as frequently happens, the getting of a clear filtrate is a long and tedious process. We have found that the only method that can be applied successfully consists in repeated filtration through the same filter. It was expected that in such a procedure, requiring more than an hour to complete, the zinc sulfide would have an excellent chance to oxidize to zinc sulfate with the result that some barium would be precipitated as barium sulfate. To test this procedure, a solution containing 100 mg. zinc as zinc nitrate, a definit quantity of barium chloride and 4 grams of ammonium chloride in a bulk of 100 cc. was heated to about 90°, made alkaline with ammonia and treated with a rapid stream of hydrogen sulfide until precipitation was complete. The precipitate was allowed to settle, care being taken to keep the solution hot by wrapping the beaker in a towel. The supernatant liquid was poured off through a double filter and the precipitate washed several times by decantation with a hot solution containing 5 per cent. ammonium nitrate and 1 per cent. ammonium sulfide and then brought on the filter. The filtrate was cloudy. It was acidified, with a slight excess of acetic acid, boiled and at the same time treated with hydrogen sulfide to prevent any possible oxidation of the sulfide to sulfate. This process had the effect of coagulating the precipitate. The liquid was then filtered through the same filter. The filtrate after two such treatments with intermediate filtrations through the same filter having failed to yield a clear filtrate, the process was again repeated, a clear filtrate now being obtained, the last portions of which drained very slowly. During the process of filtration, occupying about two hours, the precipitate was protected as much as possible from the air by covering the funnel with a watch glass. The clear filtrate was caught in an Erlenmeyer flask, boiled to expel the hydrogen sulfide and allowed to stand over night. A slight white residue which settled out was filtered off and the barium in the clear filtrate determined as barium sulfate.

The filtrate from the barium sulfate was then evaporated to a small bulk and filtered. The filtrate was made alkaline with ammonia and tested for zinc with disodium phosphate. A faint cloudiness was obtained showing that a little zinc had passed into the filtrate. It was expected that such a lengthy procedure would involve a great loss, but the figures obtained show that it was surprisingly small. The results are:

TABLE VI.—100 MG. Zn, 4 G. NH_4Cl, VOL. 100.

Ba taken. Mg.	Ba recovered. Mg.	Ba lost. Mg.
100	97.8	2.2
100	96.7	3.3
100	97.1	2.9
100	97.2	2.8
	Average loss,	2.8

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3. Sensitiveness of the Group and Confirmatory Reagents.—The failure to detect barium with ammonium carbonate may be accounted for by the fact that the solubility of barium carbonate is materially increased by the presence of ammonium salts. As these accumulate throughout the course of a systematic analysis, the test for barium in the fourth group becomes unreliable, especially for small amounts.

It may be readily seen how as much as ten grams of ammonium salts may accumulate, due to the following causes: To prevent the precipitation of 500 mg. of magnesium as magnesium hydroxide by ammonia, at least two grams of ammonium chloride must be present.[1] Ammonium salts, especially the nitrate, are added from time to time for the purpose of coagulating colloidal precipitates. The acidification of the filtrate from the third group and the subsequent neutralization give rise to still more ammonium salts. Extreme cases involving a basic acetate separation cause the amount of ammonium salts in the solution to be further increased. However, as the filtrate from the third group is generally concentrated to about 30 cc. before the alkaline earth carbonates are precipitated, the amount of ammonium salts held in solution tends to regulate itself, so that about ten grams remain.[2]

A number of experiments were made to determin the least amount of barium that could be detected under the conditions which prevail in a qualitative analysis. Solutions containing barium chloride and varying amounts of ammonium chloride in 30 cc. were heated in small (100 cc.) beakers to 60°[3] and treated with 5 cc. of reagent ammonium carbonate.[4] The solutions were then stirred vigorously and observed after two and five minutes. The results obtained were:

TABLE VII.—VOL. 30 CC., TEMP. 60° C., 5 CC. REAGENT $(NH_4)_2CO_3$.

NH_4Cl present Grams.	Least amount of Ba (mg.) detected within	
	2 min.	5 min.
0	0.8	0.5
2	3	3
5	5	5
10	10	10

These results indicate the decided influence which varying amounts of ammonium chloride have on the precipitation of small quantities of barium. It must, however, be noted that by a procedure somewhat different from that in general use, the chief features of which are the use

[1] Noyes, Bray and Spear, THIS JOURNAL, 30, 533 (1908), and confirmed by us.

[2] The solubility of ammonium chloride in cold water is 33 parts in 100.

[3] Above 60° the reagent decomposes on addition to the hot liquid.

[4] Prepared by dissolving 200 grams of Merck's reagent ammonium carbonate in 200 cc. of ammonia (sp. gr. 0.9) and then diluting the whole with water to a liter. The quantity of reagent used was sufficient to precipitate over 1400 milligrams of barium.

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of alcohol, and a large excess of ammonium carbonate which causes magnesium to be precipitated with the alkaline earths, Bray[1] has shown that a distinct test is obtained with 2 mg. Ba in less than five minutes.

A study of the potassium chromate test for barium was made under the conditions proposed by Bray[2] with the exception that the solutions were not filtered, but directly compared with a blank run under the same conditions. Our results showed that 0.4 mg. gave a distinct test while with smaller amounts no difference from the blank was noted.

4. Influence of the Presence of Impurities in the Reagents Employed throughout the Analysis.—The factor which perhaps deserves as much attention as the others is the presence of sulfates in the reagents. Many of the so-called "highest purity" reagents sold by prominent manufacturers often contains enough sulfates to make the test for barium in the fourth group a practical impossibility even though appreciable amounts of the element are present. The group reagent, ammonium carbonate, generally contains enough sulfates to cause the precipitate obtained with this reagent to be partially insoluble in acetic acid with the result that a negative test is obtained for barium with the confirmatory reagent, potassium chromate. This would account for the fact that even though an indication of the presence of the group is obtained, no test for its individual members can be gotten.

Conclusion.

A consideration of the factors studied above shows that they are typical of the conditions prevailing in actual qualitative work. In order to get a definit idea of the extent of the losses entailed by these factors they were studied from a quantitative standpoint. However, as the na ure of the work in qualitative analysis is such that the chances for mechanical losses are many, we may confidently expect that the several losses enumerated above will be greatly magnified under ordinary qualitative laboratory conditions. To test this point a number of test analyses were run. The substances analyzed were all unknown mixtures containing varying amounts of barium together with other components in proper proportions. In no case was a significant amount of barium found with ammonium carbonate although as much as 50 milligrams of the element was present in a number of the samples analyzed. With some of the substances, tests with dilute sulfuric acid were obtained where the ammonium carbonate test failed. As this reagent is capable of detecting exceedingly small[3]

[1] THIS JOURNAL, 31, 625.

[2] *Ibid.*, 31, 616 (1909).

[3] The smallest amount of barium that could be detected within 5 minutes was 0.02 mg. in the absence of ammonium salts and 0.05 mg. in a saturated solution of ammonium chloride. The tests were made on 5 cc. of solution to which 1 cc. 20 per cent. H_2SO_4 was added and the mixture boiled. The solutions were then compared with a blank run under the same conditions.

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quantities of barium the test obtained can hardly be considered conclusive except for traces.

In the light of these facts it is clear that by means of a systematic qualitative analysis it is not possible to detect barium when it occurs to the extent of 5 per cent., if a gram sample be used. This fact has led us to the task of working out another method for the systematic detection of the alkaline earth metals, which will be reported in another communication.

Summary.

It has been shown as a result of a quantitative study that in the ordinary systematic qualitative scheme the test for barium with ammonium carbonate is unreliable in consequence of losses which have been accounted for under the following heads:

1. Loss involved in the precipitation of a typical metal of the copper group, 1.4 mg. Ba.
2. Loss due to the action of ferric chloride on hydrogen sulfide, 14.0 mg. Ba.
3. Loss due to the absorption of carbon dioxide in the precipitation of the iron group with ammonia, 14.7 mg. Ba.
4. Loss involved in the precipitation of a typical metal of the ammonium sulfide group, 2.2 mg. Ba.
5. Loss involved in the precipitation and filtration of zinc sulfide, 2.8 mg. Ba.
6. Failure of the reagent ammonium carbonate to detect as much as 10 mg. barium in the presence of ammonium salts.
7. Presence of sulfates in the reagents employed.

These figures represent the minimum losses, but that they are larger in actual qualitative work is shown by the results of a number of test analyses which failed to disclose the presence of as much as 25 and in some cases 50 milligrams of barium.

METHYLENEDISALICYLIC ACID AND ITS REACTION WITH BROMINE AND IODINE.

By Erik Clemmensen and Arnold H. C. Heitman.

Received February 22, 1911.

This work was undertaken to study the interaction between methylenedisalicylic acid and iodine, and as the results were of a complicated and unexpected nature, we also included the action of bromine to see if similar or more normal conditions would prevail.

Methylenedisalicylic acid was first prepared by Geigy,[1] who obtained it by heating a mixture of salicylic acid and formaldehyde solutions with strong hydrochloric acid.

[1] D. R. P. 49970.

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It was later prepared by Kahl[1] and Madsen[2] in practically the same way. They all used a much larger amount of formaldehyde than theory calls for.

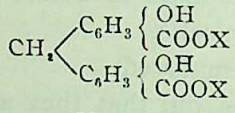
When we prepared it in the same way we obtained an impure product, which after repeated washing with hot water began to melt at 180° and only after careful purification was obtained with the correct melting point of 238°.

When we replaced strong hydrochloric acid by 50 per cent. sulfuric acid and used the theoretical amount of formaldehyde, we at once obtained a product, which after washing with hot water melted at 238°. In this connection it is worth mentioning that by carrying out the reaction in very concentrated solution, and using the theoretical amount of formaldehyde, a product is obtained which, contrary to methylenedisalicylic acid, is insoluble in cold, glacial acetic acid, and on heating does not melt but chars at a temperature above 260°, otherwise, both in reactions and empirical formula is identical with methylenedisalicylic acid.

Methylenedisalicylic acid behaves much like salicylic acid. Aqueous solutions acquire a blue coloration upon the addition of ferric salts.

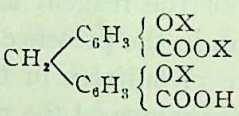
When heated above its melting point methylenedisalicylic acid is decomposed, forming hydroxyphenylmethylenesalicylic acid, and carbon dioxide, and by continued heating yields methylenediphenol.

The acid forms two kinds of salts, *viz.*:



Normal.

and



Basic.

Of the normal salts which are formed by action of carbonates on the acid, the alkali and alkali earth salts are soluble, while of the basic salts formed with excess of hydroxides, only the alkali salts are soluble.

While studying the different conditions under which formaldehyde was allowed to react on salicylic and methylenedisalicylic acids, we found that formaldehyde when in excess forms an addition product with the phenol groups of methylenedisalicylic acid from which it was readily removed by boiling the product with caustic alkalis. We were unable, however, to obtain this product sufficiently pure for analysis.

Pure methylenedisalicylic acid does not yield formaldehyde.

We observed that methylenedisalicylic acid when subjected to halogenation in alkaline solution, or in glacial acetic acid, to which mercuric oxide or acetate (serving to react with the hydrogen halide) was added,

[1] *Ber.*, 31, 148.

[2] *Arch. Pharm.*, 245, 44.

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reacted very readily with halogen, but to our surprize found that simple substitution did not follow.

Even though the results obtained in halogenating methylenedisalicylic acid were not entirely satisfactory, for the reason that the halogenated substance lacked uniformity, and that these substances or their salts could not be obtained in crystallin form, nor satisfactorily separated by fractional precipitation, or by the aid of solvents, they do nevertheless serve to indicate what follows during the reaction of methylenedisalicylic acid with bromine and iodine. Of the two, the brominated derivatives were least definit in point of substitution and distinction.

It appears, that before halogen is taken up, a condensation or rearrangement of some kind is first effected after which the halogen enters the newly formed molecule, until a certain point of saturation is reached when additional methylenedisalicylic acid is reacted upon. If, for instance, the acid was treated with halogen in such a way as would naturally introduce n atoms halogen a product would result with only $2\,n - 1/2$ atoms of halogen in the molecule. This would indicate that two molecules methylenedisalicylic acid united during the reaction forming a condensation product containing $2\,n - 1$ atoms halogen.

When a moderate amount of halogen was used, compounds of the general empirical formula $C_{30}H_{16-n}O_{10}X_n$ resulted. These compounds are dihydroxydicarboxylic acids, as with carbonates they form dibasic salts, and on treatment with hydroxides they form salts with four equivalents of base.

The acids are insoluble in water but slightly soluble in dilute mineral acids. Their alkaline solutions are strongly colored.

On acetylating, six acetyl groups are added, and these compounds when dissolved in alkalies give practically no color.

This seems to indicate that two of the hydroxyl groups are in quinoid form.

By prolonged boiling with zinc dust and potassium hydroxide all halogen is removed and compounds result with the empirical formula $C_{30}H_{16}O_{10}$, having the same general properties as the halogenated compounds.

When treated with halogen they react very readily (without the necessity of having a substance present to react with the hydrogen halide formed, as in the case of methylenedisalicylic acid) forming halogenated compounds which are identical with those obtained direct from methylenedisalicylic acid.

On heating the calcium salts of these halogenated derivatives, phenol and a small quantity of parabromocresol distil off.

When treating the halogenated dicarboxylic acids $C_{30}H_{16-n}O_{10}X_n$ with dilute alkalies or dilute mineral acids in a sealed tube at 160°, or in an alkaline solution with a large excess of halogen, carbon dioxide is

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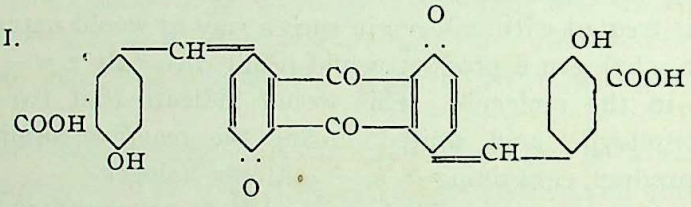
eliminated and halogenated compounds with the empirical formula $C_{29}H_{16-n}O_8X_n$ are formed.

These compounds are monobasic acids, decomposing carbonates with the formation of strongly greenish-colored insoluble salts. Upon treatment with hydroxides, they do not take up additional base nor can they be acetylated.

We were unable to completely remove the halogen from these derivatives. These halogenated monobasic acids can also be obtained direct, *viz.*: by treating methylenedisalicylic acid with a large excess of halogen in the presence of an alkaline carbonate.

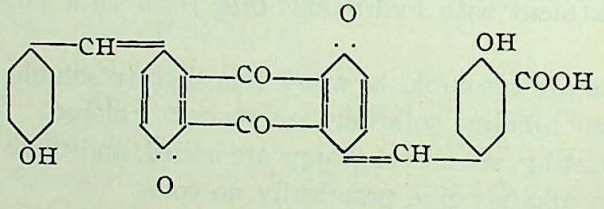
The way these compounds are obtained, and the above mentioned properties and reactions, could be explained by the following structural formulas:

I.



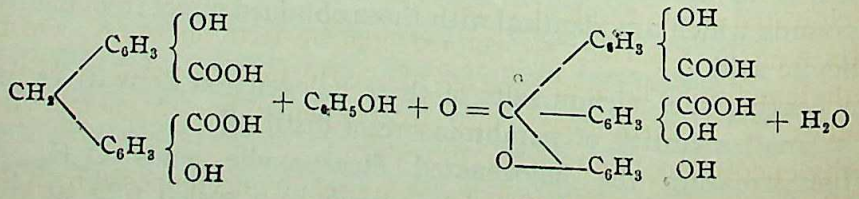
I. Representing the halogenated dihydroxydicarboxylic acids which would be designated as 1,5-anthratriquinone-4,8-dihomo-[5,5]salicylic acid.

II.



II. Representing the halogenated monocarboxylic acids, which would be designated as 4-hydroxy-8-benzylidene-1,5-anthratriquinone-4-homo-[5] salicylic acid.

Caro[1] found when reacting with an oxidizing and dehydrating mixture (nitrous acid in concentrated sulfuric acid) upon a mixture of one molecule phenol or phenolcarboxylic acid, and one molecule methylene-disalicylic acid, hydroxyaurins and their carboxylic acids are formed:

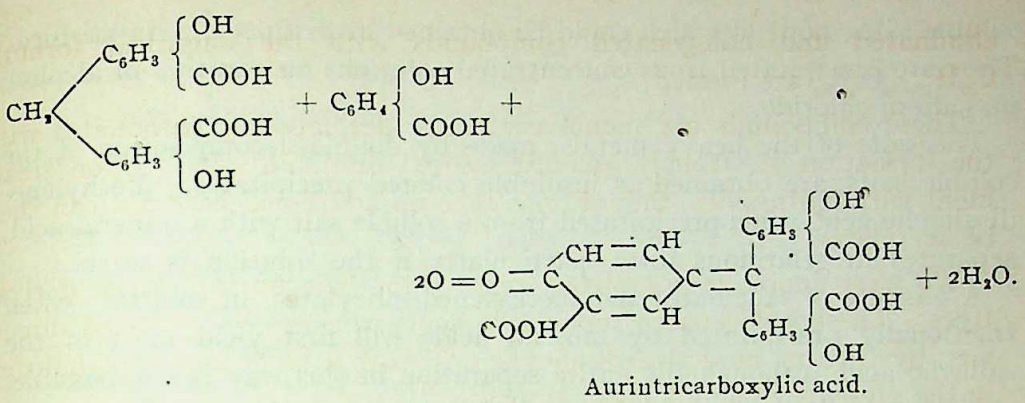


Hydroxyaurin.

[1] *Ber.*, 25, 939–943.

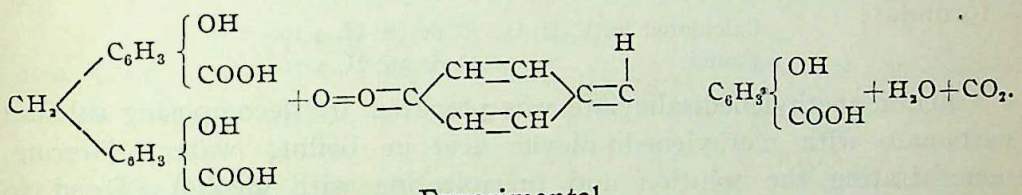
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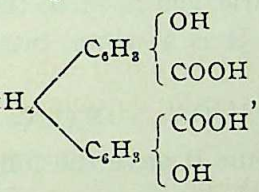


Aurintricarboxylic acid.

and Kahl[1] observed by reacting on methylenedisalicylic acid with a similar oxidizing mixture that the acid is converted into formaurin:



Experimental.

Methylenedisalicylic acid,  , was prepared by mixing 32 grams salicylic acid, 10 grams formaldehyde 40 per cent. (theory) and 180 grams 50 per cent. sulfuric acid and gently boiling the mixture 10 hours under reflux condenser. The reaction product was powdered, washed with cold water and finally several times with boiling water to remove any uncondensed salicylic acid, collected and dried. The yield was theoretical. The resulting methylenedisalicylic acid is a white powder, having a strong bitter taste and melting at 238° with decomposition. It could not be obtained in good crystallin form.

It is readily soluble in ether, acetone, alcohol, ethyl acetate, glacial acetic acid, very slightly in hot water and insoluble in benzene, chloroform, carbon disulfide and petroleum ether.

From solutions in alcohol, acetone and glacial acetic acid it is imperfectly precipitated on addition of water.

Its aqueous solutions are colored blue by ferric chloride. On heating methylenedisalicylic acid by itself above the melting point or with caustic alkalies, it is decomposed into hydroxyphenylmethylenesalicylic acid, methylenediphenol and carbon dioxide.

Alkali and alkali earth carbonates are readily decomposed by it, forming

[1] *Ber.*, 31, 143–151.

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soluble salts, none of which could be obtained in distinct crystallin form. They are precipitated from concentrated solutions on addition of alcohol, or sodium chloride.

The salts of the heavy metals, made by double decomposition of the soluble salts, are obtained as insoluble colored precipitates. Methylenedisalicylic acid, when precipitated from a soluble salt with a mineral acid, separates in gelatinous form, particularly if the solution is warm.

A mixture of salicylates and methylenedisalicylates, in solution, when fractionally precipitated by mineral acids will first yield most of the salicylic acid, although the entire separation in this way is not possible.

Methylenedisalicylic acid for analysis was prepared over the barium salt, precipitated with dilute hydrochloric acid taken up with ether, the ether evaporated and the substance dried at 100° for 5 hours.

Calculated for $C_{15}H_{12}O_6$: C, 62.48; H, 4.20.
Found: C, 62.36; H, 4.01.

Calcium methylenedisalicylate was prepared by decomposing calcium carbonate with methylenedisalicylic acid in boiling water; filtering, concentrating the solution and precipitating with alcohol. Dried to constant weight over sulfuric acid *in vacuo* the salt contains two molecules water of crystallization. It is a white, bitter-tasting substance, soluble in water.

Calculated for $C_{15}H_{10}O_6Ca + 2H_2O$: Ca, 11.07; found 11.20.

Dried at 110° for 24 hours it gave the following results:

Calculated for $C_{15}H_{10}O_6Ca$: Ca, 12.22; found, 12.54.

Dicalcium methylenedisalicylate was prepared by treating a solution of the normal calcium salt with the calculated quantity of potassium hydroxide, when the basic salt was precipitated with eight molecules water of crystallization. It is a white voluminous powder. For analysis it was dried to constant weight over sulfuric acid *in vacuo*.

Calculated for $C_{15}H_8O_6Ca_2 + 8H_2O$: Ca, 15.78; found, 15.73.

The salts of barium, magnesium and zinc were prepared and found to have the same general properties.

Barium methylenedisalicylate.....	$C_{15}H_{10}O_6Ba + 3H_2O$.
Dibarium methylenedisalicylate.....	$C_{15}H_8O_6Ba_2 + 8H_2O$.
Magnesium methylenedisalicylate.....	$C_{15}H_{10}O_6Mg + 2H_2O$.
Zinc dimethylenedisalicylate.....	$C_{15}H_{10}O_6Zn + 4H_2O$.

Diacetylmethylenedisalicylic acid was prepared by dissolving 15 grams methylenedisalicylic acid in glacial acetic acid and boiling for several hours with either 16 grams acetic anhydride or 10 grams acetyl chloride. When cold it was poured into water and separated out as a heavy oil.

It was purified by taking it up in ether, the solution washed with water, the ether evaporated and the substance dried at 50° *in vacuo* over calcium

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chloride and potassium hydroxide sticks. It is a white powder, permanent in air, melting at 142°, and decomposing carbonates forming soluble salts.

It is very soluble in ether, alcohol, acetone, acetic ether and glacial acetic acid, insoluble in water, chloroform, carbon disulfide, benzene and petroleum ether.

The substance is not colored with ferric chloride, and could not be obtained in crystallin form.

Calculated for $C_{15}H_{10}O_6(CH_3CO)_2$: C, 61.29; H, 4.33.
Found: C, 61.21; H, 4.19.

0.4484 required 48 cc. 0.1 *N* KOH corresponding to 0.4464 or 99.5% for $C_{15}H_{10}O_6(CH_3CO)_2$ with four equivalents.

Hydroxyphenylmethylenesalicylic acid, or *hydroxyphenylhomosalicylic acid*, $CH_2\begin{cases}C_6H_3\{OH,COOH\}\\C_6H_4\{OH\}\end{cases}$, was prepared by two methods: first, by dissolving 10 grams of methylenedisalicylic acid and 30 grams potassium hydroxide in 50 cc. of water, heating the mixture at 140° in a sealed tube for two hours, diluting the solution with water, filtering and saturating with carbon dioxide, extracting the separated phenols with ether and acidifying the aqueous solution with dilute hydrochloric acid, when it separated as a sticky mass; secondly, by heating methylenedisalicylic acid above its melting point for a short time, dissolving when cold in potassium hydroxide, saturating the solution with carbon dioxide, extracting with ether and acidulating.

The resulting sticky substance was taken up in ether, the solution washed well with water, the ether evaporated, and the resulting red-colored transparent mass dried at 50° *in vacuo* over calcium chloride.

It appears as a slightly red-colored electrical substance, melting above 60° and very slightly soluble in boiling water, readily soluble in ether, acetone, ethyl acetate, glacial acetic acid, and insoluble in chloroform, carbon disulfide, benzene and petroleum ether. It could not be obtained in crystallin form.

Its aqueous solution is colored blue by ferric chloride, and it decomposes alkali carbonates forming soluble salts, which are separated as viscid liquids with sodium chloride.

Calculated for $C_{14}H_{12}O_4$: C, 68.82; H, 4.95.
Found: C, 68.62; H, 5.27.

1.2580 required 50.6 cc. 0.1 *N* KOH corresponding to 1.23909 or 98.48%.

When the substance was made according to the second method, it contained small quantities of methylenedisalicylic acid. It is interesting

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to note that this substance is isomeric with the quinoid formaurin discovered by Kahl.[1]

Methylenediphenol,[2] $CH_2\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix}$, represented the major portion of the phenols which separated by saturating the potassium hydroxide solution with carbon dioxide. It was obtained pure by boiling the ether-soluble residue with water and filtering the solution hot, when on cooling it crystallized in thin colorless plates. It agrees with the properties given in the literature with one exception, having a melting point of 148° instead of 158° as given. For analysis it was dried at 100° for two hours.

Calculated for $C_{13}H_{12}O_2$: C, 77.96; H, 6.00.
Found: C, 77.40; H, 6.29.

Tribromoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{16}Br_3$, was prepared by dissolving 36 grams of methylenedisalicylic acid and 20 grams of sodium hydroxide in 1000 cc. water and adding to this a solution of 35 grams of bromine and 50 grams of sodium bromide in 500 cc. of water. The mixture was gently warmed to 45°, cooled and acidulated with dilute hydrochloric acid. The resulting reddish-colored product was washed with water, boiled with an excess of calcium carbonate suspended in dilute alcohol, and the solution filtered and concentrated, when the calcium salt separated as a dark heavy liquid. It was obtained pure by redissolving it in dilute alcohol, and concentrating the solution.

The calcium salt was decomposed with dilute hydrochloric acid and the substance taken up with ether, the ether solution washed with water, the ether evaporated and the residue dried at 100°.

It appears in the form of hard, brittle, colored lumps. When freshly prepared, it is slightly soluble in dilute mineral acids, readily in acetone, alcohol, ether and alkalies with a red color. It is insoluble in chloroform, benzene and carbon disulfide. Heated above 200° it is decomposed.

Calculated for $C_{30}H_{13}Br_3O_{10}$; Br, 31.02; found, 31.02.

The neutral calcium salt was prepared by boiling the substance with a large quantity of dilute alcohol in which finely precipitated calcium carbonate was suspended, filtering the hot solution, evaporating to one-fourth the original volume, collecting the precipitate which was first dried at ordinary temperature and finally for one hour at 100°.

It is a dark reddish-colored, hard, lumpy substance.

Calculated for $C_{30}H_{11}Br_3O_{10}Ca$; Ca, 4.93; found, 4.85.

The basic potassium salt was prepared by dissolving 9 grams of the acid in 100 cc. of alcohol containing 3.5 grams potassium hydroxide, when it was precipitated in gelatinous form. It was obtained pure by dissolving it in the least possible amount of water and precipitating with alcohol.

[1] *Ber.*, 31, 143.

[2] Beck, *Ann.*, 194, 318; Eberhardt-Welter, *Ber.*, 27, 1814; Steadel, *Ann.*, 283, 163.

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Dried at 50° over sticks of potassium hydroxide and calcium chloride *in vacuo*, it appears in the form of dark, brittle lumps soluble in water with a red color, and insoluble in acetone.

Calculated for $C_{30}H_9Br_3O_{10}K_4$: K, 16.90; found, 17.23.

Triiodoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}I_3$, was prepared by two methods: first, by dissolving 5 grams sodium hydroxide and 9 grams of methylenedisalicylic acid in 100 cc. of water, and adding this to a cold solution of 25 grams of iodine and 40 grams of sodium iodide in 1000 cc. water. The mixture was gently warmed to 80° on a steam bath, allowed to cool, the reaction product salted out with sodium chloride and acidulated with dilute sulphuric acid. Secondly, by dissolving 9 grams of methylenedisalicylic acid and 25 grams of iodine in 500 cc. of glacial acetic acid, adding 15 grams of yellow mercuric oxide, and warming the mixture to 75° until all free iodine had disappeared. The acetic acid was then removed under reduced pressure, the residue treated with sodium carbonate solution, filtered and acidulated.

The resulting iodinated product was purified by boiling it with a large quantity of dilute alcohol containing in suspension finely precipitated calcium carbonate, the clear liquid poured off, the insoluble residue collected, warmed with dilute hydrochloric acid and the insoluble product washed with water and dried. It is a reddish-colored substance, decomposing above 230° and when freshly prepared slightly soluble in dilute mineral acid and readily soluble in alcohol, acetone, ethyl acetate and glacial acetic acid. It is insoluble in water, chloroform, benzene, carbon disulfide and petroleum ether.

Alkali carbonates and alkali hydroxides yield soluble salts which dissolve with a red color.

From concentrated solutions they are precipitated in gelatinous form with alcohol.

The salts of the alkali earths and the heavy metals are insoluble in water.

Iodine is liberated by heating the substance in dry form or with concentrated sulfuric acid, and by boiling with potassium hydroxide and zinc dust it is entirely removed. When heated in a sealed tube with a one per cent. alkali carbonate or 2 per cent. mineral acid solution carbon dioxide is broken off and the substance is transformed to a monocarboxylic acid derivative. For analysis the substance was dried at 100°.

Calculated for $C_{30}H_{13}I_3O_{10}$: C, 38.84; H, 1.43; I, 42.05.
Found: C, 39.07; H, 1.67; I, 41.48.

The calcium and basic potassium salts made in the usual manner gave the following results:

Calculated for $C_{30}H_{11}I_3O_{10}Ca$: Ca, 4.20; found, 3.78.
Calculated for $C_{30}H_9I_3O_{10}K_4$: K, 14.67; found, 14.38.

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An acetylated product was prepared by boiling for 5 hours 9 grams of the substance with 10 grams of acetic anhydride dissolved in 200 cc. glacial acetic acid. The reaction mixture was poured into water, the precipitate collected, dissolved in alcohol and precipitated with water, collected and dried over potassium hydroxide sticks *in vacuo*. It is then obtained as a yellow substance, soluble in alcohol, ether, ethyl acetate and glacial acetic acid, and insoluble in benzene, chloroform, and petroleum ether.

Calculated for $C_{30}H_{11}I_3O_{10}(CH_3CO)_6$: I, 32.50; found, 31.32.

During acetylation the substance lost iodine, but it shows that a change from a quinoid configuration to a regular form has resulted and that the acetyl radical has also entered the methylene group.

Heptabromoanthratriquinonedihomosalicylic acid, $C_{30}H_9O_{10}Br_7$, was prepared by dissolving 18 grams of methylenedisalicylic acid and 10 grams of sodium hydroxide in 800 cc. water and then adding 12 grams of sodium carbonate. This solution was added to 500 cc. of water containing 60 grams of bromine and 80 grams of sodium bromide, and the mixture slowly warmed to 60°, when the reaction product separated as a yellow mass, which was collected and extracted with alcohol, the alcohol-insoluble residue dissolved in acetone and precipitated from the acetone solution with alcohol, collected and dried at 80°. The yield was 4 grams.

It is a light yellow fine, electrical powder, decomposing above 200°.

It is very soluble in acetone, slightly soluble in alcohol, and insoluble in chloroform, benzene, carbon disulfide and petroleum ether. Alkalies dissolve it with a red color. It could not be acetylated without decomposition.

Calculated for $C_{30}H_9Br_7O_{10}$: Br, 51.41; found, 50.80.

A basic potassium salt was prepared by dissolving 6 grams of the acid in 20 cc. of acetone and adding it to a solution of 1.7 grams potassium hydroxide in absolute alcohol.

The resulting dark, gelatinous substance was dissolved in the least possible amount of warm water and precipitated with absolute alcohol, collected and dried over potassium hydroxide sticks *in vacuo*, at 50°.

It appears in the form of dark-colored brittle lumps, soluble in water and insoluble in alcohol and acetone.

Calculated for $C_{30}H_5Br_7O_{10}K_4$: K, 12.72; found, 12.62.

Pentabromohydroxybenzylideneanthratriquinonehomosalicylic acid, $C_{29}H_{11}O_8Br_5$, was prepared by dissolving 18 grams of methylenedisalicylic acid, 10 grams of sodium hydroxide and 90 grams of sodium borate in 1000 cc. of water and adding the solution to 120 grams of bromine and 150 grams of sodium bromide in 1000 cc. of water. The mixture was gradually warmed to 75°, when a strong reaction followed, after which

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the yellow reaction product was collected and purified by dissolving it in acetone and precipitating with alcohol.

It is a yellow powder, practically insoluble, except in acetone and caustic alkalies. It is not precipitated from the latter solution with carbon dioxide.

When a warm acetone solution is treated with warm benzene and the solvent allowed to evaporate at ordinary temperature, a deposit is formed, which under the microscope appears to consist of small round plates.

For analysis it was dried at 100°.

Calculated for $C_{29}H_{11}Br_5O_8$: Br, 45.12; C, 39.29; H, 1.14.
Found: Br, 45.90; C, 38.47; H, 1.91.

Pentaiodohydroxybenzylideneanthratriquinonehomosalicylic acid, $C_{29}H_{11}O_8I_5$, was obtained in a similar manner, by treating methylene disalicylic acid in alkaline solution with an excess of iodine in the presence of sodium borate.

The resulting iodinated substance was purified by boiling it with very dilute (0.5 per cent.) potassium hydroxide solution, washing the greenish-colored potassium salt until the washings were neutral to litmus paper, and acidulating with dilute hydrochloric acid. The product was thoroughly washed with water and alcohol successively, collected, and dried at 100°.

The substance is a reddish-yellow colored, amorphous powder, practically insoluble in all ordinary solvents, possessing a slight quinonelike odor. On heating it does not melt, but yields iodine and a phenol, leaving a charred residue.

Iodine is also liberated on heating with concentrated sulfuric acid. Alkalies do not remove the iodine but form insoluble greenish-colored salts. All efforts to acetylate the product failed, even with sulfuric acid present. By suspending the substance in glacial acetic acid and boiling for 48 hours with concentrated hydriodic acid, a tarlike mass soluble in caustic alkalies was obtained.

Calculated for $C_{29}H_{11}O_8I_5$: C, 31.03; H, 0.99; I, 56.58.
Found: C, 31.12; H, 1.66; I, 56.49.

$C_{28}H_{10}O_6I_5COOK$. This potassium salt was prepared by two methods, first by warming the substance with an excess of dilute potassium hydroxide; and second with an excess of potassium carbonate. The greenish-colored product was collected and dried. It is an olive-green insoluble powder, permanent in the air.

The analyses of the substance obtained by both methods are given.

Calculated for $C_{29}H_{10}O_8I_5K$: K, 3.37. Found: 1, 4.20; 2, 3.14.

Anthratriquinonedihomosalicylic acid, $C_{30}H_{16}O_{10}$, was prepared by boiling the tribromo derivative with 600 cc. of 25 per cent. potassium hydroxide and 200 grams zinc dust under reflux condenser for 24 hours.

The cold reaction mixture was diluted with water, filtered, acidulated

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with 50 per cent. sulfuric acid, when the dehalogenated substance separated, as a white precipitate which darkened rapidly on exposure to air. By dissolving it in acetone and precipitating with water it was obtained as a brown powder, which decomposes at 185° and behaves like the original halogenated substance.

Dissolved in glacial acetic acid and treated with bromine or iodine, substitution follows, yielding halogenated products similar to those obtained by treating methylenedisalicylic acid with halogen in the presence of a neutralizing substance.

Calculated for $C_{30}H_{16}O_{10}$: C, 67.15; H, 3.01.
Found: C, 66.55; H, 3.98.

The calcium salt and basic potassium salt were made in the same manner and had the same general properties as the salts of the original halogenated substance. The analyses gave the following results:

Calculated for $C_{30}H_{14}O_{10}Ca$: Ca, 6.98; found, 7.08.
Calculated for $C_{30}H_{12}O_{10}K_4$: K, 22.72; found, 21.95.

The ethyl ester of anthratriquinonedihomosalicylic acid was prepared by heating the silver salt with an excess of ethyl iodide and absolute alcohol in a sealed tube for 5 hours at 160°. The alcohol and excess of ethyl iodide were evaporated, the sustance taken up in ether, the solution washed with potassium carbonate and the ether evaporated. The ester was then obtained as a colorless, resinous mass which in contradistinction to the acid was soluble in benzene but could not be obtained in crystallin form.

In the hope of getting a crystallin acetyl derivative the ester was treated with a large excess of acetic anhydride and the resulting product in ether solution washed with potassium carbonate and the ether evaporated.

The acetylated ester was then obtained as a brown solid which melts above 70° to a liquid possessing a slight ethereal odor. It could however not be crystallized.

It is very soluble in alcohol, acetone, benzene, chloroform, ether and ethyl acetate, only slightly so in carbon disulfide and insoluble in petroleum ether.

Calculated for $C_{28}H_{12}O_6(CH_3CO)_6(COOC_2H_5)_2$: C, 66.80; H, 3.51.
Found: C, 66.02; H, 5.06.

The acetylated derivative must therefore be hexaacetyldihydroxy anthraquinone dihomoethylsalicylate.

40 grams of the calcium salt of the tribromo derivative was mixed with an equal quantity of potassium carbonate and subjected to dry distillation, when 12 grams of phenols distilled. They were fractionated, 75 per cent. coming over at 180–185° while the last fraction distilled above 220°. The first fraction was identified as phenol, and the second as bromoparacresol.

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Summary.

1. Methylenedisalicylic acid is obtained pure and in good yield by the interaction of formaldehyde and salicylic acid in molecular proportions, in the presence of 50 per cent. sulfuric acid.

2. Heated above the melting point methylenedisalicylic acid decomposes into hydroxyphenylmethylenesalicylic acid, methylenediphenol and carbon dioxide.

3. When treated with bromine or iodine, methylenedisalicylic acid as such is not halogenated.

4. The action of bromine or iodine on methylenedisalicylic acid effects a condensation in which two molecules of acid are involved, resulting in the formation of a molecule which may be designated as a halogenated anthratriquinonedihomosalicylic acid.

5. This was dehalogenated with zinc dust and potassium hydroxide.

6. When halogenated anthratriquinonedihomosalicylic acid is heated with a solution of alkaline carbonates or mineral acids, under pressure, it is decomposed yielding a monobasic acid, which may be considered as halogenated hydroxybenzylideneanthratriquinonehomosalicylic acid.

7. Halogenated hydroxybenzylideneanthratriquinonehomosalicylic acid is also formed by reacting on methylenedisalicylic acid with a large excess of halogen in the presence of a neutralizing substance like borax or an alkaline carbonate.

LABORATORIES OF PARKE, DAVIS & CO.,
DETROIT.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

SYNTHESES OF PYRROLE COMPOUNDS FROM IMIDO ACIDS. *N*-PHENYL-α,α'-DICARBETHOXY-β,β'-DIKETOPYRROLIDINE.

BY TREAT B. JOHNSON AND ROBERT BENGIS.

Received March 13, 1911.

In a paper entitled "Researches on Furfurans," Johnson and Johns[1] showed that diethyl diglycolate condenses with diethyl oxalate, in the presence of sodium ethylate, giving practically a quantitative yield of 2,5-dicarbethoxy-3,4-diketotetrahydrofurfurane (II). The formation of this cyclic compound, in this manner, was perfectly analogous to that of dimethyl diketocamphorate (I)[2] from diethyl oxalate and dimethyl β,β-dimethylglutarate. The authors also stated, in this same paper, their intention of continuing this work and also of examining the behavior of diethyl oxalate towards esters of thiodiglycolic and diglycolamidic acids. These esters would be expected to condense in a manner similar to the glutarates or diglycolates giving the corresponding diketotetrahy-

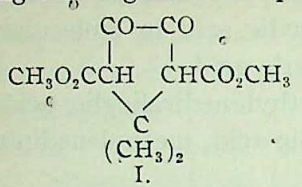
[1] *Am. Chem. J.*, 31, 290 (1906).

[2] Komppa, *Ber.*, 32, 1421; 34, 2472; 36, 4332; Dieckmann, *Ibid.*, 32, 1933.

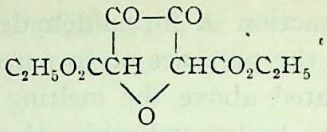
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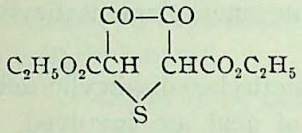
drothiophenes (III), and diketopyrrolidines (IV)[1] respectively. Results confirming our original assumptions have been described in a recent paper



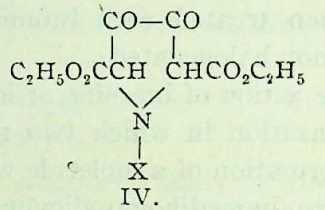
I.



II.



III.



IV.

by Hinsberg,[2] in which he has shown that diethyl oxalate condenses smoothly with diethyl thiodiglycolate giving the thiophene (III). He furthermore describes several thiophene derivatives which were obtained by condensing the thiodiglycolate with certain α-ketone esters and o-diketones. In this paper we shall describe a general method of synthesizing pyrrolidines of the general formula (IV). The study of these pyrrole compounds is of especial interest because of their unique properties and also because of their possible use for further syntheses. Their investigation will be continued.

A careful review of the literature, before we undertook this investigation, revealed the fact that the action of diethyl oxalate on a diglycolamidate had previously been examined. The results of this work are described in a paper entitled "The Condensation of Phenylglycinoacetic Esters in Presence of Sodium Alkyloxides," by Mouilpied,[3] in which he discusses the action of oxalic esters on esters of *N*-phenyldiglycolamidic acid in the presence of sodium alcoholates. The authors' conclusions, however, seemed so improbable to the writer that we deemed it necessary to repeat some of his experiments.

Mouilpied[4] observed that diethyl oxalate condenses smoothly with diethyl *N*-phenyldiglycolamidate, in the presence of sodium ethylate, giving a compound having the same empirical formula as *N*-phenyl α,α-dicarbethoxy-β,β'-diketopyrrolidine (V) and melting at 137°. He did not however assign a pyrrole structure to the condensation product because it did not undergo saponification under normal conditions and did

[1] "These compounds are structurally represented throughout this paper as ketone compounds or pyrrolidines. They might also be represented in their tautomeric form or as hydroxyl derivatives of pyrrole and, in fact, this *enol* constitution is indicated by their acid character and by many of their reactions." (T. B. J.)

[2] *Ber.*, 43, 901 (1910).

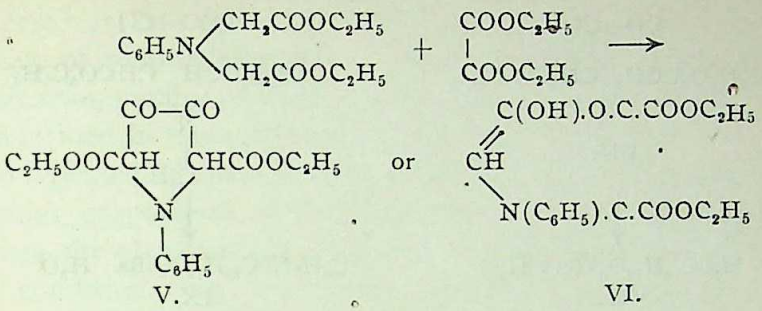
[3] *J. Chem. Soc.*, 87, 435.

[4] *Loc. cit.*

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not react with hydroxylamine or phenylhydrazine giving an oxime and phenylhydrazone respectively. He discusses the possibility of the



V. VI.

compound having a quinoid structure, VI, because it gives a yellow sodium salt, and finally concludes that a satisfactory, constitutional formula cannot be established.

We have now re-examined this compound of Mouilpied's melting at 137°, and have obtained evidence which we believe proves that this substance has not the quinoid formula VI and have therefore assigned to it the constitution of an oxypyrrolidine as represented by the formula V. The fact that the compound does not undergo saponification normally, does not preclude the structure of a pyrrole compound. The stability of this substance, in the presence of alkali and acids, might be predicted. Johnson and Johns[1] observed this same stability in the case of the corresponding tetrahydrofurfurane (II), and Hinsberg[1] makes the following statement regarding the stability of the tetrahydrothiophene (III). "Der Dioxy-thiophendicarbonsäureester wird beim kochen mit überschüssigem Alkali bedeutend schwieriger verseift—offenbar, weil die beiden Hydroxylgruppen einen schützenden Einfluss auf die benachbarten Carboxymethyl-Gruppen ausüben." A lactone ring as represented by the quinoid formula VI would be expected to undergo saponification very easily. That the compound does not react with hydroxylamine and phenylhydrazine is very probably due to the fact that it functionates here as a hydroxyl compound instead of an *o*-diketone.

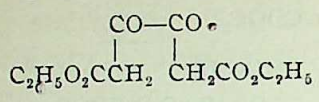
If Mouilpied's condensation product, melting at 137°, has a quinoid structure (VI), it would contain only one acid hydrogen atom, and therefore give only a mono-sodium salt. We now find that this substance dissolves in alkali giving a characteristic disodium salt, which is yellow in color and very soluble in water. It reacted smoothly with para-nitrobenzyl chloride giving a dialkyl derivative, insoluble in alkali, and combined with the required amount of barium chloride giving a quantitative yield of a mono-barium salt containing one molecule of water of crystallization (IX). This latter observation is significant because the corresponding acyclic compound, diethyl ketipate (VII), gives an analogous

[1] *Loc. cit.*

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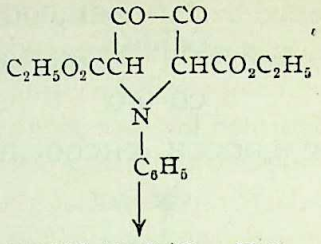
yellow barium salt (VIII), containing also one molecule of water.[1] Their relationship is shown by the following formulas:



VII.



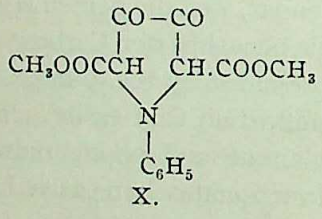
VIII.



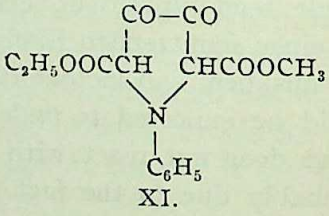
IX.

When this yellow disodium salt was digested in alcohol with the hydrochloride of an aromatic base (aniline, phenylenediamine, etc.) only one atom of sodium was displaced by hydrogen, and a quantitative yield of the mono-sodium salt was obtained. This salt is difficultly soluble in cold water, is colorless, and dissolves in sodium hydroxide solution, giving a deep yellow solution of the disodium salt. It is our intention to study further these interesting sodium salts and also the corresponding potassium salts.

The interesting observation was also made by Mouilpied that, while diethyl oxalate and diethyl *N*-phenyldiglycolamidate condense in the presence of sodium ethylate giving the pyrrolidine melting at 137°, if the same esters are condensed in the presence of sodium methylate, this compound is not obtained, but the corresponding dimethyl ester (X), melting at 188°, is formed. This interesting result led him to carry out



X.



XI.

all the possible condensations of the dimethyl and diethyl esters of oxalic and *N*-phenyldiglycolamidic acids in the presence of sodium ethylate and sodium methylate. Among these eight possible condensations, he observed the formation of the compound melting at 137° in only the one case mentioned above. Identical condensation products, melting at 146–7°, were obtained by condensation of dimethyl oxalate with diethyl *N*-phenyldiglycolamidate and diethyl oxalate with dimethyl *N*-phenyldiglycolamidate in the presence of sodium ethylate. On the other hand when these esters were condensed in the same order, in the presence of sodium methylate, the product of the two reactions melted at 188°. Diethyl and dimethyl oxalates condensed with diethyl and dimethyl

[1] Fittig, Daimler and Keller, *Ann.*, 249, 193.

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N-phenyldiglycolamidates, respectively, in the presence of sodium methylate, giving compounds melting at 175° and 195°. On the other hand, dimethyl oxalate and dimethyl *N*-phenyldiglycolamidate gave, in the presence of sodium ethylate, a product melting at 159°. Therefore, six different compounds, melting at 137°, 146–7°, 159°, 175°, 188° and 195°, were formed in these eight condensations.

We have repeated all these possible condensations and used in each case two molecular proportions of the alcoholate, but are unable to confirm in every case the observations of Mouilpied. We succeeded in isolating, in a pure condition, only two definit condensation products, *viz.*: *N-phenyl-α,α'-dicarbethoxy-β,β'-diketopyrrolidine* melting at 137° and the corresponding dimethyl ester (X), melting at 188–9°. Mouilpied intimates that his compounds may possibly be structural isomers, but the results obtained by us indicate that the condensation products melting at 146–7°, 159° and 175° are only indefinit mixtures of the pyrrolidines melting at 137° and 188° and not definit compounds. In no case did we obtain a substance melting at 195°. It is possible that one of the compounds described by Mouilpied was the mixed ethyl methyl ester represented by formula XI.

Our results show conclusively that the constitution of the product of these reactions is determined by the structure of the alcoholate used in the condensation, and not by that of the esters used. If sodium ethylate is employed, a diethyl ester of the pyrrolidine is formed and a dimethyl ester is obtained if sodium methylate is used. Our results are perfectly analogous with those described by other investigators who have observed similar metathetical changes.[1]

Experimental Part.

The *N*-phenyldiglycolamidic acid $C_6H_5N(CH_2COOH)_2$,[2] which was used in this work, was prepared according to the following directions: One hundred and twelve grams of chloroacetic acid were dissolved in 100 cc. of water and this solution added to a mixture of 300 cc. of water and two hundred and ninety-six grams of anhydrous sodium carbonate. This mixture was then heated in an oil bath to 80° and ninety-three grams of phenylglycine added in small portions so as to avoid too violent an effervescence of carbon dioxide. After heating two hours at 110–120°, the solution was cooled to 0° and the diglycolamidic acid precipitated by careful addition of an excess of hydrochloric acid. If insufficient acid is added, a mono-sodium salt of the diglycolamidic acid separates. The yield obtained by this procedure was about 80–85 per cent. of the theoretical

[1] Purdie, *Ber.*, 26, 1554. Israel, *Ann.*, 231, 220. Peters, *Ibid.*, 257, 353. Leuchs and Theodoresen, *Ber.*, 43, 1239. Hinsberg, *Ibid.*, 43, 904. Dieckmann, *Ibid.*, 43, 1028. Komnenos, *Monatsh.*, 31, 111, 687; 32, 77. Pfannl, *Ibid.*, 31, 301

[2] Hansdörfer, *Ber.*, 22, 1798; 23, 1990.

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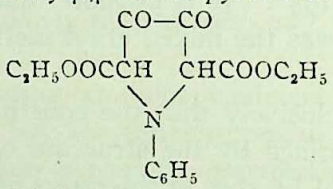
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and the acid generally melted at 152–155° with effervescence without further purification.

Diethyl N-phenyldiglycolamidate, $C_6H_5N(CH_2COOC_2H_5)_2$,[1] and *dimethyl N-phenyldiglycolamidate*, $C_6H_5N(CH_2COOCH_3)_2$.[2] These esters can easily be prepared by esterification of the diglycolamidic acid in the usual way, in presence of hydrochloric or sulfuric acid. The simplest method however is to dissolve fifty grams of the acids in about 150 cc. of the absolute alcohol and after the addition of 15 cc. of concentrated sulfuric acid, to digest on the steam bath for seven to eight hours. The excess of alcohol is then removed by heating at 50° under diminished pressure, the ester washed with dilute sodium carbonate solution, dissolved in ether and dried over anhydrous sodium sulfate. They are then purified by distillation under diminished pressure, the ethyl ester boiled at 200–206° at 6 mm. and the methyl ester at 216–218° at 25 mm.

Condensations in the Presence of Sodium Ethylate.

N-Phenyl-α,α'-dicarbethoxy-β,β'-diketopyrrolidine.



I. By Condensation of Diethyl Oxalate with Diethyl-N-phenyldiglycolamidate.

One and two-tenths grams of sodium were dissolved in 50 grams of boiling, absolute alcohol and the solution cooled. A mixture of 6.7 grams of diethyl *N*-phenyldiglycolamidate and 3.7 grams of diethyl oxalate were then added at once to the ethylate, when a violent reaction set in, by gentle warming, with evolution of heat and formation of a yellow disodium salt of the pyrrolidine. After heating at 100° for 3–4 hours, to complete the reaction, the salt was dissolved in cold water, the solution washed with ether to remove a trace of oil and the pyrrolidine precipitated by addition of an excess of hydrochloric acid. The pyrrolidine separated at once in yellow, prismatic crystals, which melted at 135°. It crystallized from hot alcohol or glacial acetic acid in beautiful needle-like prisms which melted at 137–8° to a clear oil without effervescence. The yield was 7.5 grams or 93.7 per cent. of theory. The yield of the pyrrolidine was diminished by condensing the esters in more dilute solutions of sodium ethylate. Analysis (Kjeldahl):

Calculated for $C_{16}H_{17}O_6N$: N, 4.39. Found: N, 4.8; 4.46.

II. By Condensation of Diethyl-N-phenyldiglycolamidate with Dimethyl Oxalate.

[1] Bischoff, *Ber.*, 30, 2309.

[2] Mouilpied, *Loc. cit.*

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Molecular proportions of the two esters were condensed under the same conditions as described in the preceding experiment. The reaction was complete after heating for 15 minutes and a homogeneous disodium salt was obtained. The diethyl ester separated at once on adding hydrochloric acid to an aqueous solution of the salt and melted at 133–5°. After two crystallizations from 95 per cent. alcohol, it melted constant at 137°. Analysis (Kjeldahl):

Calculated for $C_{10}H_{17}O_6N$: N, 4.39. Found: N, 4.2.

III. By Condensation of Dimethyl N-Phenyldiglycolamidate with Diethyl Oxalate.

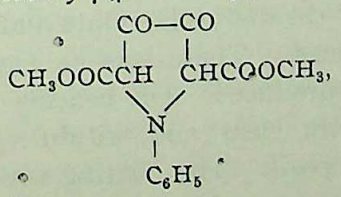
In this experiment, we obtained from 1.85 grams of the oxalate and 3.0 grams of the diglycolamidate, 2.2 grams of the diketopyrrolidine, melting at 135–7°. The alcoholic filtrates, after purification of the cyclic ester, were concentrated and cooled, when a crystallin product separated, which melted at about 147° to an oil. This melting point was assigned by Mouilpied[1] to the compound obtained by condensation of the above esters in presence of sodium ethylate. An examination of this material, however, showed that it was not a definit substance, but a mixture, apparently, of two compounds crystallizing in needles and stout, well-developed prisms. The needles predominated and, after being separated mechanically from the prisms, melted at 136°. A sufficient quantity of the prisms for safe identification was not obtained.

IV. By Condensation of Dimethyl N-Phenyldiglycolamidate with Dimethyl Oxalate.

By proceeding in exactly the same manner as in the three preceding experiments we obtained, in this case, a product which melted before purification at about 143–5° to a turbid oil. After two crystallizations, however, from 95 per cent. alcohol, the pure cyclic diethyl ester was obtained and melted sharply at 136–7°. A mixture of this substance and the ester from Experiment I melted at exactly the same temperature. Mouilpied states that the product of the condensation, in this case, melts at 159°. An attempt to convert the diethyl ester, melting at 137°, into the corresponding dimethyl ester (see below) by digestion with a methyl alcohol solution of sodium was unsuccessful. It was recovered unaltered after digestion for five hours.

Condensations in the Presence of Sodium Methylate.

N-Phenyl-α,α′-dicarbmethoxy-β,β′-diketopyrrolidine,



[1] *Loc. cit.*

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I. By Condensation of Dimethyl N-Phenyldiglycolamidate with Dimethyl Oxalate.

The formation of this cyclic dimethyl ester, in this experiment and the three following, was not as smooth as that of the corresponding diethyl ester. Two-tenths of a gram of sodium was dissolved in 7 cc. of dry methyl alcohol, the solution cooled and a mixture of 2 grams of the dimethyl diglycolamidate and 1 gram of dimethyl oxalate added at once. The reaction was not vigorous and only a faint turbidity was produced. After heating on the steam bath for 6–7 hours, a heavy, yellow salt was obtained, insoluble in the alcohol. This was dissolved in water, washed with ether, and the solution acidified with hydrochloric acid. The dimethyl ester separated at once and was purified for analysis by cystallization from hot alcohol. It separated on cooling in well-defined prismatic crystals, which melted at 188–189° to a clear red oil. Analysis (Kjeldahl):

Calculated for $C_{14}H_{13}O_6N$: N, 4.81. Found: N, 4.49; 4.63.

II. By Condensation of Dimethyl N-Phenyldiglycolamidate with Diethyl Oxalate.

We used in this experiment 3.0 grams of the diglycolamidate, 1.85 grams of the oxalate and 0.6 gram of sodium dissolved in 9 cc. of methyl alcohol. The product of the condensation was crystallized once from 95 per cent. alcohol, when we obtained 1.7 grams of the pure cyclic dimethyl ester melting at 188–9°. When the alcoholic filtrate was concentrated and cooled, a substance separated, which melted at 177° to a turbid oil. An examination of this material under the microscope, however, showed that it was a mixture. By recrystallizations from alcohol the melting point was finally raised to 181°, indicating the cyclic dimethyl ester. The impurity removed by this treatment was, without doubt, a trace of the cyclic diethyl ester melting at 137°. Analysis (Kjeldahl):

Calculated for $C_{14}H_{13}O_6N$: N, 4.81. Found: N, 4.63.

III. By Condensation of Diethyl N-Phenyldiglycolamidate with Dimethyl Oxalate.

The only product identified in this experiment was the cyclic dimethyl ester melting at 188–9°.

IV. By Condensation of Diethyl N-Phenyldiglycolamidate with Diethyl Oxalate.

In this experiment 0.4 gram of sodium was dissolved in 5 cc. of methyl alcohol and 2.0 grams of the diglycolamidate and 1.1 grams of the oxalate added in the usual manner. There was no vigorous reaction and only a slight turbidity was produced. On heating on the steam bath, the solution became perfectly clear and within 15–20 minutes, a yellow sodium salt began to deposit. The heating was continued for one hour and the salt then dissolved in cold water, the solution filtered and acidi-

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fied with hydrochloric acid. A colorless crystallin compound separated at once. It crystallized from alcohol in prismatic crystals and was identified as the cyclic dimethyl ester melting at 188–9° to a clear oil. The yield was excellent. Analysis (Kjeldahl):

Calculated for $C_{14}H_{13}O_6N$: N, 4.81. Found: N, 4.68.

When the alcoholic filtrates were concentrated, a substance separated, on cooling, which melted at 157–166°. The appearance of this material under the microscope, however, was similar to that observed in the previous experiments, a mixture of needles and stout prisms. A definit compound could not be obtained by repeated crystallizations from alcohol and the crystallin appearance of the product obtained indicated a mixture of the cyclic diethyl ester melting at 137° and the methyl ester melting at 188–9°. Mouilpied states that the product of the condensation in this case is a compound melting at 175°.

The melting points of the various condensation products obtained by Mouilpied[1] and us, in the eight experiments described above, are given for comparison in the following table. The temperatures 137° and 188–9° are the melting points of *N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine* and *N-phenyl-α,α'-dicarbmethoxy-β,β'-diketopyrrolidine*, respectively.

TABLE I.

	N-Phenyldiglycolamidate.	Oxalic ester.	Alcoholate.	Mouilpied's melting point.	Our melting point.
1.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOC_2H_5)_2$	C_2H_5ONa	137°	137°
2.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOC_2H_5)_2$	C_2H_5ONa	146–7°	137°
3.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOC_2H_5)_2$	C_2H_5ONa	147°	137°
4.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOCH_3)_2$	C_2H_5ONa	159°	137°
5.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOC_2H_5)_2$	CH_3ONa	175°	188–189°
6.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOCH_3)_2$	CH_3ONa	188°	188–189°
7.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOC_2H_5)_2$	CH_3ONa	188°	188–189°
8.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOCH_3)_2$	CH_3ONa	195°	188–189°

The Sodium Salts of N-Phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine. This pyrrolidine gives two characteristic sodium salts: a disodium salt which is yellow and a monosodium salt which is colorless. The yellow salt is always formed by dissolving the ketone in aqueous alkali or by adding the pyrrolidine to alcohol containing the required proportion of sodium ethylate. It then separates as a bright yellow powder insoluble in boiling alcohol. Especially interesting is the behavior of this yellow salt when digested in alcohol with an excess of a halide of an aromatic base, *viz.*: aniline, toluidine, or phenylenediamine hydrochlorides. By this treatment, only one of the sodium atoms of the salt is displaced and a quantitative yield of the colorless monosodium salt is obtained. This salt is practically insoluble in alcohol and difficultly soluble in water, giving a neutral solution. It decomposes when heated above 260° and dissolves

[1] *Loc. cit.*

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at once in warm, dilute sodium hydroxide solution giving the characteristic yellow solution of the disodium salt. When the salt was triturated with dilute hydrochloric acid, the N-phenyl α,α' dicarbethoxy-β,β'-diketopyrrolidine separated and after one crystallization from alcohol melted at 137° to a clear oil. Nitrogen determination, (Kjeldahl):

Calculated for $C_{16}H_{16}O_6NNa$: N, 4.10. Found: N, 4.5.

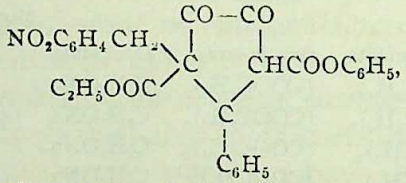
Barium Salt of N-phenyl α,α'-dicarbethoxy β,β'-diketopyrrolidine,

$C_6H_5N(C(COOC_2H_5)CO)_2.Ba.H_2O$.

The diethyl ester was dissolved in water with two molecular proportions of potassium or sodium hydroxide and a slight excess of barium chloride added to the solution. The barium salt separated at once as a fine, yellow powder. After heating a few minutes to complete the reaction, the salt was filtered off, washed with hot water to remove any barium chloride and finally with alcohol. The salt is practically insoluble in these two solvents. It contained one molecule of water of crystallization, which it did not lose by standing in a desiccator over concentrated sulfuric acid.

Calculated for $C_{16}H_{15}O_6NBa.H_2O$: H_2O, 3.81; Ba, 29.02.
Found: H_2O (at 100-110°), 3.89; Ba, 28.50, 29.1.

N-Phenyl α,α'-dicarbethoxy-α-paranitrobenzyl-β,β'-diketopyrrolidine,



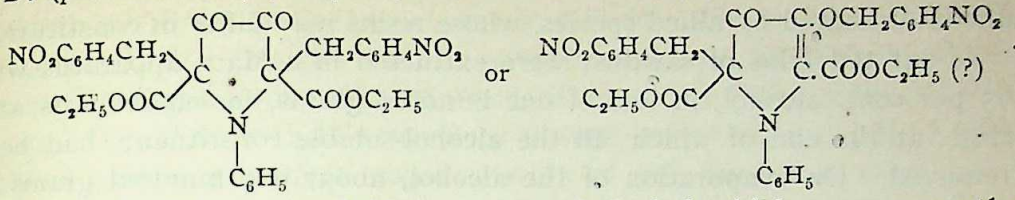
The yellow disodium salt of the diketopyrrolidine was first prepared, in the usual manner, by dissolving 3.0 grams of the diethyl ester in alcohol containing the required amount of sodium (0.43 gram). The theoretical quantity of nitrobenzyl chloride was then added and the mixture digested on the steam-bath until the solution gave no alkaline reaction when tested with turmeric. After evaporation of the excess of alcohol at ordinary temperature, the crude reaction product remained as a red semi-solid, which was pasty after standing exposed to the air for several hours. This was first triturated with warm water to remove sodium chloride and the oily residue, insoluble in water, then finally triturated with cold alcohol and the material undissolved by this treatment saved (see below). When the water and alcohol solutions were allowed to concentrate by slow evaporation, the mono-paranitrobenzyl derivative separated as an orange-colored powder, resembling, in appearance, pulverized potassium dichromate. It was soluble in dilute alkali and melted at 180–182° to a bright red oil with slight effervescence. The yield was small. Analysis (Kjeldahl):

Calculated for $C_{23}H_{22}O_8N_2$: N, 6.16. Found: N, 5.87; 6.24.

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Di-(paranitrobenzyl)-N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine,



The residue (above) insoluble in water and alcohol, which was apparently the chief product of the reaction, dissolved immediately in glacial acetic acid. When allowed to stand for about two days, the diparanitrobenzyl derivative finally separated in yellow prisms, which melted quite sharp at 132° to a clear oil. This compound was very soluble in boiling alcohol and separated, on cooling, in needle-like prisms which melted at 131–2° to a clear oil. It was insoluble in alkali and a mixture of the compound and the unaltered diethyl ester (m. p. 137°) melted at 109°. Nitrogen determination (Kjeldahl):

Calculated for $C_{30}H_{27}O_{10}N_3$: N, 7.13. Found: N, 6.98.

Behavior of N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine towards Hydriodic Acid and Aluminium Amalgam.

Two attempts to reduce this compound with these reagents were unsuccessful. There was no evidence of saponification or reduction after boiling 3.0 grams of the pyrrolidine with 5 cc. of the acid for several minutes. It apparently underwent only slight decomposition by careful treatment and after being separated from the acid and decolorizing with a little sulfur dioxide water, it melted at 135–7° to an oil. By prolonged digestion, the ester was charred and was completely decomposed.

In a second experiment, the pyrrolidine was dissolved in 95 per cent. alcohol and the solution poured upon a large excess of aluminium-amalgam. After allowing to stand for 8–9 hours, when the evolution of hydrogen had ceased, the alcohol solution was filtered, concentrated and cooled. The unaltered diketopyrrolidine separated in needles and melted at 136–7°.

NEW HAVEN, CONN.

A SESQUITERPENE AND AN OLEFINIC CAMPHOR OCCURRING IN SOUTHERN CYPRESS.[1]

BY ALLAN F. ODELL.

Received March 9, 1911.

While conducting a series of experiments on the oxidation products of sawdust, it was observed that the ethereal extract from the aqueous oxidation mixture of cypress sawdust left upon evaporation a very fragrant residue. The constant recurrence of this odor in connection with cypress wood led to an investigation of its nature.

The cypress in this section is entirely of the species *Taxodium distichum*,

[1] Paper read before the New Orleans Section, March 17, 1911.

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consequently the sawdust, obtained from shingle mills, must have been uncontaminated by allied species, whose resins may differ in constitution.

About ten kilos of sawdust were extracted in a Marx apparatus with 95 per cent. alcohol, in lots of one hundred grams, for eight hours at a time, at the end of which all the alcohol-soluble constituents had been removed. On evaporation of the alcohol, about one hundred grams of a red, viscous resin were left. This was subjected to fractional distillation, at first in a vacuum, but afterward, on account of foaming in the distillation flask, it was found to succeed better by first distilling off the traces of the alcohol and water, to which the resin clung tenaciously at atmospheric pressure, and then fractionating the residue in a vacuum of 35 mm.

The first fraction came over between 180–190°, and consisted of 8 cc. of a light yellow, and very fragrant oil, which gives undoubtedly the essential odor of cypress, though in its concentrated condition it recalled the odor of vanilla somewhat.

The second fraction was collected between 217–222°, and consisted of about 50 cc. of a yellow, very viscous oil, smelling of empyreumatic products, and within twenty-four hours, resinifying to such an extent as to be entirely opaque and dark brown.

There were signs of a yet higher fraction, boiling between 235–245°, but the quantity was so small that it could not be purified with certainty. That which was obtained, solidified on cooling to a clear amber-colored, semi-solid mass.

The fraction boiling between 217–222° presented considerable difficulty in its purification, as the empyreumatic odor and the tendency to resinify were only removed after repeated fractionation, by which the original yield of oil was considerably reduced.

One very pure specimen was obtained by distillation in a cathode vacuum, in which its boiling point was reduced to 125°.

The oil was finally obtained as a yellowish-green, viscous, and almost odorless product, boiling at $218–220°_{35}$, and $295–300°_{778}$, and showing no resinification after standing in the light for a month.

Carbon and hydrogen were found on testing, and a combustion made with the Dennstedt apparatus gave C, 88.46; H, 11.20 per cent. The cryoscopic method gave a lowering corresponding to a molecular weight of 207. The Landesberger method gave an elevation corresponding to a molecular weight of 209, which would determin the compound as a sesquiterpene, $C_{15}H_{24}$.

The specific gravity was found to be $0.9647\ {}^{18°}_{4°}$; $n_D^{22°}$ 1.5240. The calculated molecular refractivity is 62.55, that found by the Lorenz-Lorentz formula is 64.66; the difference is slightly greater than the increase due to one ethylene linkage.

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Its solution in carbon tetrachloride absorbs two molecules of bromine, and there occurs at the same time a variable amount of substitution.

It was at first thought that this sesquiterpene was an impure specimen of cadinene on account of its conduct with moderately concentrated nitric acid. Its action with this was very violent, and yielded a yellow amorphous oxidation product, together with an acid similar in odor to isovaleric. This yellow substance dissolved in potassium hydroxide to a red solution, and evolved a very fragrant ethereal odor on boiling. The solution of the sesquiterpene, however, in either chloroform or acetic acid, yielded an intense red color immediately on the addition of conc. sulfuric acid, and no intermediate green or blue as in the case of cadinene. Nor was there any appearance of violet as in the case of carrapene. The fact was later established that the compound contained only one ethylene linkage, which classes it with the somewhat rare tricyclic terpenes.[1]

It is dextrorotatory, $[\alpha]_D^{20} = +6.53°$ in a 10 cm. tube of the pure substance.

The properties of this compound are not characteristic of any other of the known tricyclic sesquiterpenes, and the name *cypressene* will be given to it to distinguish it in future investigations.

Preliminary experiments upon its oxidation yielded as products much carbon dioxide, and a considerable amount of the ill-smelling acid before mentioned, together with a compound, the nature of which has not been satisfactorily established.

All efforts to obtain the hydrochloride have, as yet, resulted in failure.

The fraction of the resin which distilled between 180–190° was refractionated, and though the quantity was small, a fairly pure distillate was obtained, boiling from 182–185°$_{35}$. It came over as a light yellow, very fragrant, mobil oil, which on combustion yielded the following: C, 80.28; H, 10.96; O, 8.76 per cent. The Landesberger method gave an elevation corresponding to a molecular weight of 182, giving to the substance the formula $C_{12}H_{20}O$.

Its density is $0.9469^{20°}_{4°}$, n_D^{20} 1.5040. The calculated molecular refractivity, in 53.16, that found by the Lorenz-Lorentz formula, is 56.29; the difference corresponds to two ethylene linkages within the limits of error.

Its solution in carbon tetrachloride adds four molecules of bromine, which result is in harmony with that obtained from its molecular refractivity.

The substance is probably an aldehyde, as it reduces ammoniacal silver nitrate solution readily; and it restores the color to decolorized fuchsin solution. It gives a precipitate when its alcoholic solution is boiled with an alcoholic solution of resorcinol and the mixture is poured into water.

[1] *Chem. Zentr.*, 1901, II, 1226.

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It was slightly resinified by boiling with potassium hydroxide solution, but it failed to reduce Fehling's solution even upon continued boiling.

The quantity was not large enough to determin satisfactorily whether a sulfite compound was formed or not, and the attempt to prepare a small quantity of the semicarbazone was unsuccessful.

It is dextrorotatory.

An aldehyde with the formula $C_{12}H_{20}O$, with two ethylene linkages, would be an olefin, homologous with geraniol. The name *cypral* will be given to this compound, as at present no such homolog of the olefinic camphors is known.

As circumstances have made necessary the postponement of this work for several months, the details so far gathered have been given in this paper for the interest of those engaged in terpene investigations.

Summary.

The summary of the physical properties of the two new compounds described is as follows:

Cypressene, $C_{15}H_{24}$, a yellowish-green, viscous, and almost odorless oil, b. p. 218-220°$_{35}$ and 295–300°$_{778}$. Sp. gr. $0.9647^{18}/_{4}$. n_D^{22} 1.5240. $[\alpha]_D^{20} = 6.53°$. *Cypral*, $C_{12}H_{20}O$, a light yellow, mobil, and very fragrant oil of b. p. 182–185°$_{35}$. Sp. gr. $0.9469^{20}/_{4}$. n_D^{20} 1.5040. Dextrorotatory.

LOUISIANA STATE UNIVERSITY,
BATON ROUGE, LA.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

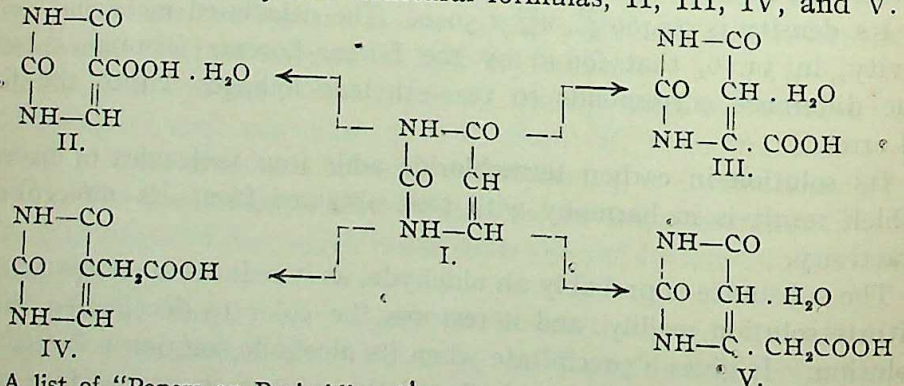
RESEARCHES ON PYRIMIDINES: SYNTHESIS OF CYTOSINE-5-ACETIC ACID.

[FIFTY-FIRST PAPER.] [1]

BY TREAT B. JOHNSON (Experimental work by HARLEY T. PECK and JOSEPH A. AMBLER).

Received March 21, 1911.

If one considers only the carbon-substitution products of uracil (I), there are two possible uracilcarboxylic and two uracilacetic acids. They are represented by the structural formulas, II, III, IV, and V.



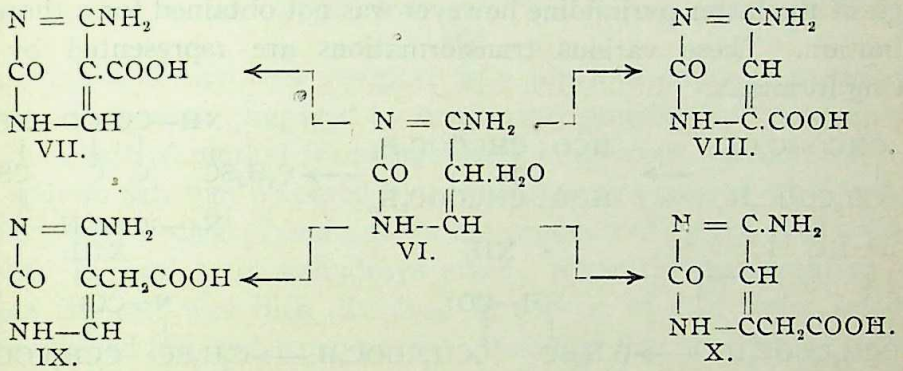
[1] A list of "Papers on Pyrimidines," previously published from this laboratory, is appended to this paper.

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Three of these have been synthesized in this laboratory, *viz.*: uracil-5-carboxylic acid[1] (II), uracil-5-acetic acid[2] (IV) and uracil-4-acetic acid[3] (V). The last member of the series, or uracil-4-carboxylic acid (III), was prepared by Müller[4] and its constitution later definitly established by Wheeler.[5]

Of the four corresponding acids of cytosine (VI), only one has previously been described, *viz.*: cytosine-5-carboxylic acid (VII), which was synthesized by Wheeler and Johns.[6] A description of the synthesis and properties of cytosine-5-acetic acid (IX) will be given in this paper.



Johnson and Speh[7] have shown that the sodium salt of diethyl formylsuccinate (XI) condenses smoothly with pseudoethylthiourea, in aqueous solution, giving ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate (XV). We now find that this mercaptopyrimidine (XV) reacts with phosphorus oxychloride under proper conditions, without destruction of the ester grouping, giving an excellent yield of ethyl 2-ethylmercapto-6-chlorpyrimidine-5-acetate (XVI). Especially interesting was the behavior of this chloride towards ammonia. The corresponding aminopyrimidine (XIX) was not obtained as expected, but it underwent an inner condensation giving smoothly the γ-lactam of 2-ethylmercapto-6-amino-pyrimidine-5-acetic acid (XVIII), with formation of a molecule of alcohol. This cyclic compound underwent hydrolysis easily, by heating with concentrated hydrochloric acid, giving practically a quantitative yield of the hydrochloride of cytosine-5-acetic acid (XX). The free acid was then obtained by treatment of this salt with one molecular proportion of alkali in aqueous solution.

Thiourea and diethyl formylsuccinate condensed smoothly, in the presence of sodium ethylate, giving a good yield of ethyl 2-thio-6-oxypyrimi-

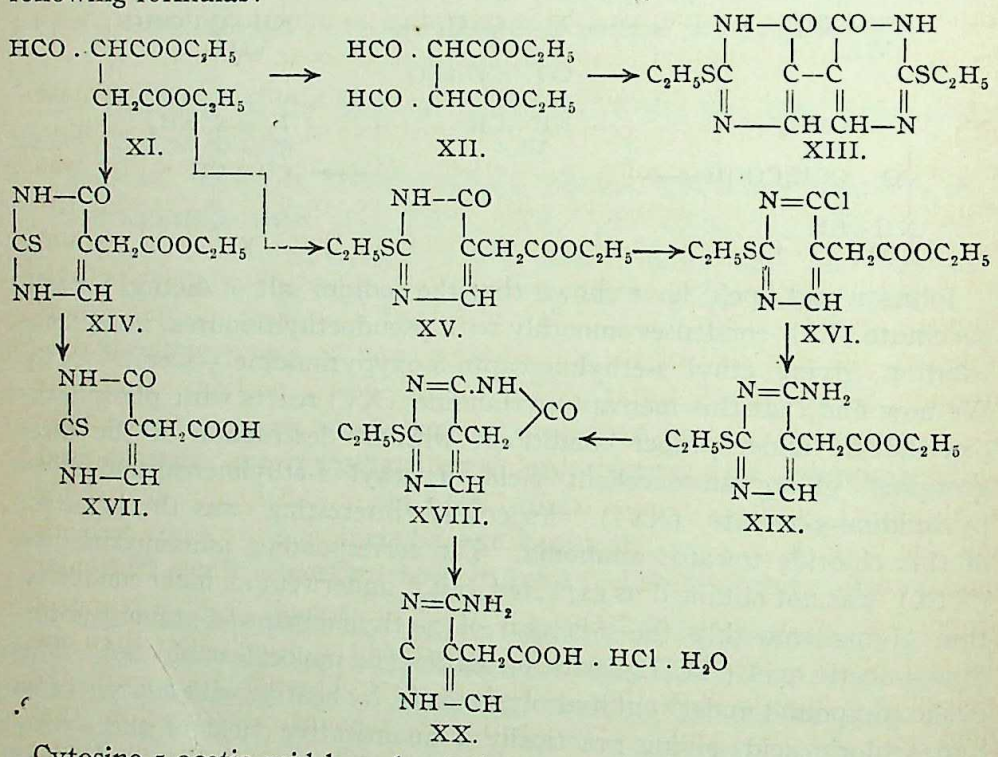
[1] Wheeler, Johnson and Johns, *Am. Chem. J.*, 37, 392.
[2] Johnson and Speh, *Ibid.*, 38, 602.
[3] Wheeler and Liddle, THIS JOURNAL, 30, 1156.
[4] *J. prakt. Chem.*, 56, 488.
[5] *Am. Chem. J.*, 38, 358.
[6] *Ibid.*, 38, 595.
[7] *Loc. cit.*

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dine-5-acetate (XIV). When this was saponified with alkali the corresponding acetic acid (XVII) was obtained.

Diethyl succinate apparently can condense with two molecular proportions of ethyl formate giving the disodium salt of diethyl diformylsuccinate (XII). The yield however is very small. Its formation was shown by the fact that the condensation product of pseudoethylthiourea and sodium diethylformylsuccinate was, in two experiments, a mixture of ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate (XV), and a difficultly soluble substance having the composition of the dipyrimidine (XIII). Enough of the latter pyrimidine however was not obtained for a thorough examination. These various transformations are represented by the following formulas:



Cytosine-5-acetic acid has about the same solubility in water as uracil, thymine or uracil-5-acetic acid (IV). Like its lower homolog, cytosine-5-carboxylic,[1] it crystallizes from water in an anhydrous condition. Cytosine,[2] on the other hand, crystallizes with one molecule of water. This property of these cytosine acids to crystallize from water in an anhydrous condition is worthy of attention. Uracil crystallizes from water in anhydrous form while, on the other hand, every acid of the series represented above, *viz.*: (II), (III), (IV) and (V), crystallizes with one molecule of water, with the exception of uracil-5-acetic acid (IV). Cytosine-5-

[1] *Loc. cit.*

[2] Weeler and Johnson, *Am. Chem. J.*, 29, 492.

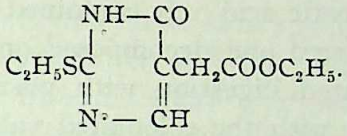
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acetic acid is not precipitated from an aqueous solution of its hydrochloride by phosphotungstic acid, while cytosine is practically quantitatively precipitated with this reagent. The acid like cytosine-5-carboxylic acid[1] forms a characteristic monohydrochloride, which crystallizes with one molecule of water.

Experimental Part.

Ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate,



This compound has been described in a previous paper from this laboratory.[2] It is easily prepared by condensing pseudoethylthiourea with the sodium salt of diethyl formylsuccinate in aqueous solution.

The sodium salt was prepared by condensing 45 grams of ethyl formate with 100 grams of diethyl succinate in the presence of 13 grams of sodium, suspended in 150 cc. of anhydrous ether. After the condensation was complete the salt was then dissolved in 600 cc. of cold water and the solution divided into two equal parts. Assuming that the yield of sodium salt was theoretical (129 grams), a molecular proportion of pseudoethylthiourea hydrobromide (53 grams), dissolved in 100 cc. of water, was added to the first half of the salt solution, and 27 grams of the hydrobromide, in 100 cc. of water, added to the second portion. Molecular proportions of potassium hydroxide (16 and 8 grams) were then finally added to combine with the hydrobromic acid and the two solutions allowed to stand, at ordinary temperature, for 12 hours and finally heated for half an hour at 100°. After cooling and acidifying the solutions with glacial acetic acid, we obtained from the first fraction in which molecular proportions were used 30 grams and from the second part 18 grams of the mercaptopyrimidine. In another experiment, in which more than one molecular proportion of the pseudourea hydrobromide was used, the yield was not increased. The experiments demonstrate therefore that the yield of pyrimidine is decreased by using less than one molecular proportion of the hydrobromide for a condensation. A yield of 30 grams of the mercaptopyrimidine from 50 grams of diethyl succinate corresponds to 43.2 per cent. of the theoretical.

In one experiment 20 grams of diethyl succinate were condensed with 17 grams of ethyl formate (2 mols.) in presence of 6.0 grams of sodium suspended in ether. After standing for 5 days the crude salt was dissolved in 125 cc. of water and 42 grams of the hydrobromide of pseudoethylthiourea, dissolved in 75 cc. of water, added to the solution. Thirteen

[1] *Loc. cit.*

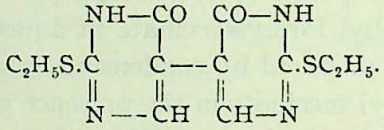
[2] Johnson and Speh, *Loc. cit.*

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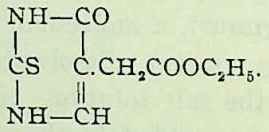
grams of potassium hydroxide, in 20 cc. of water, were then added and the solution allowed to stand for 13–14 hours. After heating half an hour to complete the reaction, cooling and acidifying with acetic acid, we obtained a heavy deposit of ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate mixed with a small amount of a fine crystallin powder. This was separated by trituration of the crude reaction product with warm alcohol. The compound was insoluble in this solvent and water and difficultly soluble in acetic acid. It contained sulfur and had no definit melting point but charred and decomposed on heating. It was purified for analysis by repeated digestion with glacial acetic acid. Nitrogen determinations agreed with the calculated value for

2,-Diethylmercapto-6,-dioxy-5,5-dipyrimidine,



Calculated for $C_{12}H_{14}O_2N_4S_2$: N, 18.06; found, 17.70, 17.95.

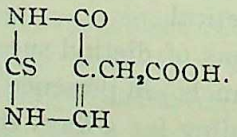
Ethyl 2-thio-6-oxypyrimidine-5-acetate,



The sodium salt of diethyl formylsuccinate was prepared in the usual manner by condensation of 20 grams of diethyl succinate with 9 grams of ethyl formate in presence of 2.6 grams of sodium. After dissolving in 120 cc. of cold water, 8 grams of thiourea, in 75 cc. of water, were added to the solution and the mixture allowed to stand about 10 hours. It was then heated on the steambath for half an hour, cooled and acidified with glacial acetic acid. Eight grams of the thiopyrimidine separated as a yellow crystallin powder. The pyrimidine was purified by crystallization from hot water and separated in prismatic crystals melting at 178–180°. Analysis (Kjeldahl):

Calculated for $C_8H_{10}O_3N_2S$: N, 13.08; found, 13.09, 13.04.

2-Thio-6-oxypyrimidine-5-acetic acid,



The potassium salt of this acid was obtained by saponification of the preceding ethyl ester with aqueous potassium hydroxide. When the alkaline solution was acidified with hydrochloric acid this pyrimidine separated in prismatic crystals. The yield was quantitative. It is purified

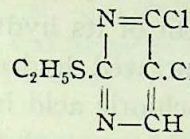
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best by crystallization from hot water and melts with decomposition at ±260°, according to the rate of heating. Analysis (Kjeldahl):

Calculated for $C_6H_6O_3N_2S$: N, 15.05; found, 14.85, 15.00.

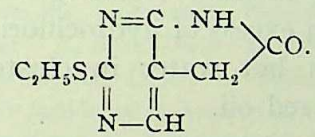
Ethyl 2-ethylmercapto-6-chloropyrimidine-5-acetate,



Fifteen grams of ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate were dissolved in 50 cc. of phosphorus oxychloride and digested for half an hour when the evolution of hydrochloric acid practically ceased. The excess of chloride was then removed by distillation under diminished pressure when we obtained a sirupy liquid, which was poured upon crushed ice to decompose any phosphorus halide present. The pyrimidine separated as an oil insoluble in water and was dissolved in ether and dried over calcium chloride. It boiled at 220° at 31 mm. pressure. The yield of purified oil was 7 grams or about 44 per cent. of theory. In two other experiments, in which we used 30 grams of the mercaptopyrimidine and 75 cc. of the phosphorus halide, we obtained 15 and 14 grams of the chloride boiling at 203–203.5° at 16 mm. and 215° at 28 mm. pressure respectively. Analysis (Kjeldahl):

Calculated for $C_{10}H_{13}O_2SCl$: N, 10.74; found, 11.0, 10.50.

γ-Lactam of 2-ethylmercapto-6-aminopyrimidine-5-acetic acid or 2-ethylmercapto-5,6-(α-pyrrolidone)-pyrimidine,



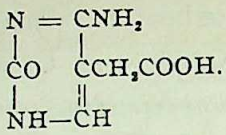
This pyrimidine was obtained, in an attempt to prepare ethyl 2-ethylmercapto-6-aminopyrimidine-5-acetate, by heating ethyl 2-ethylmercapto-6-chloropyrimidine-5-acetate with ammonia. Fifteen grams of the 6-chloropyrimidine were dissolved in 100 cc. of strong alcoholic ammonia and heated for 5 hours at 120–130°. When the tube was opened a crystallin substance was suspended in the alcohol mixed with ammonium chloride. The alcohol was removed by evaporation on the steambath and the product obtained triturated with cold water to dissolve the ammonium chloride. The undissolved pyrimidine was then dissolved in hot alcohol and the solution cooled, when it separated as a red granular powder which melted at 208°. The yield was good. The compound is difficultly soluble in water and soluble in acids. Analysis (Kjeldahl):

Calculated for $C_{10}H_{15}O_2N_3S$: N, 17.42.
Calculated for $C_8H_9ON_3S$: N, 21.54.
Found: I, 21.57; II, 21.62.

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Cytosine-5-acetic acid,



This acid was obtained in the form of its hydrochloride by hydrolysis of the above γ-lactam with concentrated hydrochloric acid. The salt crystallizes from 20 per cent. hydrochloric acid in minute needles, which decompose at 135–140° with effervescence, and contain one molecule of water of crystallization, $C_6H_7O_3N_3.HCl.H_2O$. Water determination:

Calculated for $C_6H_7O_3N_3.HCl.H_2O$: H_2O, 8.05; found, 8.3.

Chlorine determination in hydrous salt:

Calculated for $C_6H_7O_3N_3.HCl.H_2O$: Cl, 15.88; found, 15.95, 16.04.

Cytosine-5-acetic acid was obtained by dissolving this hydrochloride in the required volume of 0.1 *N* sodium hydroxide solution and heating to boiling temperature. On cooling, the acid deposited in granular, orange-colored crystals. After decolorization with bone-coal the acid is colorless and blackens in a capillary tube at 240–250°, but does not melt below 290°. The acid was dried for analysis in a desiccator over calcium chloride. It does not contain water of crystallization. One hundred grams of water dissolve at 25° 0.3373 gram of the acid. Analysis (Kjeldahl):

Calculated for $C_6H_7O_3N_3$: N, 24.85; found, 24.62, 25.01, 24.86.

Cytosine-5-acetic acid is not precipitated from an aqueous solution of its hydrochloride by addition of phosphotungstic acid, mercuric chloride or copper sulfate. Potassio-bismuth iodide gives an amorphous precipitate which dissolves in an excess of hydrochloric acid.

Picrate.—Crystallizes from hot water in clusters of needles, which melt at 217–218° to a dark red oil.

Addenda.

For the sake of reference, a complete list of the papers on pyrimidines, which have been published from this laboratory, is given below. These papers are arranged in the order in which they appeared.

1. Researches on the Cycloamidines: Pyrimidine Derivatives. By Henry L. Wheeler. *Am. Chem. J.*, 20, 481.

2. On Some Condensation Products of the Pseudothioureas: Synthesis of Uracil, Thymine and Similar Compounds. By Henry L. Wheeler and Henry F. Merriam. *Am. Chem. J.*, 29, 478.

3. Synthesis of Amino-oxypyrimidines Having the Composition of Cytosine: 2-Amino-6-oxypyrimidine and 2-Oxy-6-aminopyrimidine. By Henry L. Wheeler and Treat B. Johnson. *Am. Chem. J.*, 29, 492.

4. On Cytosine or 2-Oxy-6-aminopyrimidine from Triticonucleic Acid. By Henry L. Wheeler and Treat B. Johnson. *Am. Chem. J.*, 29, 505.

5. 5-Methylcytosine. By Henry L. Wheeler and Treat B. Johnson. *Am. Chem. J.*, 31, 591.

6. Synthesis of 2-Amino-5-methyl-6-oxypyrimidine. By Treat B. Johnson and Samuel H. Clapp. *Am. Chem. J.*, 32, 130.

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7. 2-Oxy-4,6-Diaminopyrimidine. By Henry L. Wheeler and George S. Jamieson. *Am. Chem. J.*, 32, 342.

8. The Structure of Some Substitution Products. By Henry L. Wheeler and H. Stanley Bristol. *Am. Chem. J.*, 33, 437.

9. The Action of Potassium Thiocyanate upon Some Imide Chlorides. By Henry L. Wheeler and H. Stanley Bristol. *Am. Chem. J.*, 33, 448.

10. The Action of Aqueous and Alcoholic Ammonia and Aniline on Some Halogen and Mercapto Pyrimidines. By Treat B. Johnson and Carl O. Johns. *Am. Chem. J.*, 34, 175.

11. 2-Ethylmercapto-5-amino-6-oxypyrimidine. By Treat B. Johnson. *Am. Chem. J.*, 34, 191.

12. On 2,5-Diamino-6-oxypyrimidine. By Treat B. Johnson and Carl O. Johns. *Am. Chem. J.*, 34, 554.

13. Some 5-Iodopyrimidine Derivatives: 5-Iodocytosine. By Treat B. Johnson and Carl O. Johns. *J. Biol. Chem.*, 1, 305.

14. On Methods of Synthesizing Isobarbituric Acid and 5-Oxycytosine. By Treat B. Johnson and Elmer V. McCollum. *J. Biol. Chem.*, 1, 437.

15. The Action of Potassium Thiocyanate upon Imide Chlorides. By Treat B. Johnson and Elmer V. McCollum. *Am. Chem. J.*, 36, 136.

16. On the Formation of Purines from Ureapyrimidines. By Treat B. Johnson and Elmer V. McCollum. *Am. Chem. J.*, 36, 149.

17. On 5-Nitrocytosine and its Reduction to 2-Oxy-5,6-diaminopyrimidine. By Treat B. Johnson, Carl O. Johns and Frederick W. Heyl. *Am. Chem. J.*, 36, 160.

18. 5-Ethylcytosine. By Treat B. Johnson and George A. Menge. *J. Biol. Chem.*, 2, 105.

19. Synthesis of Uracil-5-carboxylic Acid. By Henry L. Wheeler, Treat B. Johnson and Carl O. Johns. *Am. Chem. J.*, 37, 392.

20. On a Color Test for Uracil and Cytosine. By Henry L. Wheeler and Treat B. Johnson. *J. Biol. Chem.*, 3, 183.

21. On Some Salts of Cytosine, Isocytosine, 6-Aminopyrimidine and 6-Oxypyrimidine. By Henry L. Wheeler. *J. Biol. Chem.*, 3, 285.

22. Uracil-4-carboxylic Acid. By Henry L. Wheeler. *Am. Chem. J.*, 38, 358.

23. The Action of Methyl Iodide on 2-Anilino-6-oxypyrimidine, and the Synthesis of 2-Anilinopyrimidine. By Treat B. Johnson and Frederick W. Heyl. *Am. Chem. J.*, 38, 237.

24. Synthesis of Thymine-4-carboxylic Acid. By Treat B. Johnson. *J. Biol. Chem.*, 3, 299.

25. Synthesis of Cytosine-5-carboxylic Acid. By Henry L. Wheeler and Carl O. Johns. *Am. Chem. J.*, 38, 594.

26. Synthesis of Thymine-5'-carboxylic Acid. By Treat B. Johnson and Carl Frank Speh. *Am. Chem. J.*, 38, 602.

27. Synthesis of 4-Methyluracil-5-acetic Acid. By Treat B. Johnson and Frederick W. Heyl. *Am. Chem. J.*, 38, 659.

28. A Method of Separating Thymine from Uracil. By Treat B. Johnson. *J. Biol. Chem.*, 4, 407.

29. The Action of Nitric Acid on 2,6-Dioxypyrimidines. Oxynitrohydrothymine. By Treat B. Johnson. *Am. Chem. J.*, 40, 19.

30. Synthesis of Uracil-3-acetic Acid. By Henry L. Wheeler and Lenoard M. Liddle. THIS JOURNAL, 30, 1152.

31. Synthesis of Uracil-4-acetic Acid. By Henry L. Wheeler and Leonard M. Liddle. THIS JOURNAL, 30, 1156.

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32. Synthesis of Some Nitrogen Alkyl Derivatives of Cytosine, Thymine and Uracil. By Treat B. Johnson and Samuel H. Clapp. *J. Biol. Chem.*, 5, 49.

33. The Action of Diazo-Benzene Sulfonic Acid on Thymine, Uracil and Cytosine. By Treat B. Johnson and Samuel H. Clapp. *J. Biol. Chem.*, 5, 163.

34. The Action of Potassium Thiocyanate upon Some Imide Chlorides. By Treat B. Johnson and Walter F. Storey. *Am. Chem. J.*, 40, 131.

35. Synthesis of Cytosine-5-carboxamide. By Henry L. Wheeler and Carl O. Johns. *Am. Chem. J.*, 40, 233.

36. Synthesis of 4-Methylcytosine. By Carl O. Johns. *Am. Chem. J.*, 40, 348.

37. On Some Picrolonates. By Henry L. Wheeler and George S. Jamieson. *J. Biol. Chem.*, 4, 111.

38. Synthesis of Some Benzyl Derivatives of Uracil and Thymine. By Treat B. Johnson and John H. Derby, Jr. *Am. Chem. J.*, 40, 444.

39. Synthesis of New Derivatives of 5-Hydroxyuracil (Isobarbituric Acid). By Treat B. Johnson and D. Breese Jones. *Am. Chem. J.*, 40, 538.

40. The Thio Derivatives of Uracil and the Preparation of Uracil in Quantity. By Henry L. Wheeler and Leonard M. Liddle. *Am. Chem. J.*, 40, 548.

41. On the Formation of Purine Derivatives from 4-Methylcytosine. By Carl O. Johns. *Am. Chem. J.*, 41, 58.

42. Synthesis of 1-Methyl-5-hydroxyuracil. By Treat B. Johnson and D. Breese Jones. THIS JOURNAL, 31, 591.

43. The Preparation of 3-Methyl- and 3-Benzyluracil. By Henry L. Wheeler and Treat B. Johnson. *Am. Chem. J.*, 42, 30.

44. The Preparation of 1,4-Dimethyluracil and of the Monobenzyl derivatives of 4-Methyluracil. By Henry L. Wheeler and David F. McFarland. *Am. Chem. J.*, 42, 101.

45. Sulphur Derivatives of 5-Hydroxyuracil: Preparation of 5-Benzylmercaptouracil and 5-Benzylmercaptocytosine. By Treat B. Johnson and Herbert H. Guest. *Am. Chem. J.*, 42, 271.

46. Dimethyl Derivatives of 2–Aminopyrimidine, Preparation of 2-Methylamino-5-methylpyrimidine. By Treat B. Johnson and Kenneth G. Mackenzie. *Am. Chem. J.*, 42, 353.

47. The Action of Methyl Iodide, and of Benzyl Chloride upon 2-Oxy-4-methyl-6-mercaptopyrimidine. By Henry L. Wheeler and David F. McFarland. *Am. Chem. J.*, 42, 431.

48. Synthesis of 5-Cyanuracil. By Treat B. Johnson. *Am. Chem. J.*, 42, 505.

49. The Thio Derivatives of Thymine and the Preparation of Thymine. By Henry L. Wheeler and David F. McFarland. *Am. Chem. J.*, 43, 19.

50. The Condensation of Thiourea with Esters of Allylmalonic and Some Alkyl Substituted Allylmalonic Acids. By Treat B. Johnson and Arthur J. Hill. *Am. Chem. J.*, 45, 356.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 189.]

A TETRA-ACETYL AMINOGLUCOSIDE.

BY MARSTON LOVELL HAMLIN.

Received March 27, 1911.

A preliminary report of work on chitin begun independently last October, suggested in part by investigations of Offer[1] as to the structure of chitin,

[1] *Biochem. Z.*, 7, 117.

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was just ready for publication when Irvine, McNicoll and Hynd[1] published an article reporting nearly identical experiments covering the same field. This paper is therefore published as corroborative of their work, with which it agrees on all points that are common.

The triacetylbromoglucosamine hydrobromide described in the present paper is evidently identical with the compound prepared by these authors, but the acetylated glucoside now reported is, I believe, new.

The investigation consisted in preparing a bromoacetyl derivative of glucosamine and from this an acetylated aminoglucoside. This is apparently not a derivative of the aminoglucoside recently prepared by Fischer and Zach[2] in quite a different way, since the latter on hydrolysis gave the hydrochloride of an amino sugar different in behavior from glucosamine hydrochloride.

Experimental.

1-Bromo-3,5,6-triacetylglucosamine Hydrobromide. — This compound was prepared in a way analogous to that in which Koenig and Knorr[3] made bromoacetylglucose; the reaction, however, can be carried out at a higher temperature, and goes very quickly.

Five grams of finely powdered free glucosamine, prepared according to Breuer,[4] were placed in a small flask connected with a reflux condenser, and 25 cc. Kahlbaum's acetyl bromide added, the flask being cooled by ice and water. A lively effervescence set in at once, due to the evolution of hydrobromic acid gas. After about ten minutes most of the solid went into a brown solution, which in about five minutes more suddenly became solid. The excess of acetyl bromide was sucked off by a vacuum pump at room temperature for $^1/_2$–1 hour, the residue dissolved in boiling chloroform, the brown solution filtered and allowed to cool, dry ether added till no more precipitate formed and, after a little standing, the white precipitate, tinged slightly brown, was filtered off on a Büchner funnel. The substance is pure enough at this point to use in preparing the glucoside, if the chloroform solution was not allowed to stand over night. All the apparatus must be thoroughly dry, and during the experiment the reflux condenser must be protected with a calcium chloride tube.

For analysis this precipitate was crystallized twice more in the same way, the product being a fine, pure white powder. Bromine was determined by dissolving this in water, adding nitric acid and boiling, then adding silver nitrate and weighing the precipitate as usual.

[1] *J. Chem. Soc.*, 99, 250 (1911).
[2] *Ber.*, 44, 132 (1911).
[3] *Ibid.*, 34, 957 (1901).
[4] *Ibid.*, 31, 2193 (1898).

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	Br.
Calculated for $C_6H_9O_4Ac_3BrN,HBr$:	35.63
Found: Sample I, *a*.	35.36
b.	35.43
Sample II, *a*.	35.55
b.	35.59

For this compound the following structure seems probable:

$$CH_2OAc.CHOAc.\overset{\Big\lceil\!\!\Big\rceil}{CH}.CHOAc.CHNH_2.CHBr.$$
$$\Big\lceil\!\!\Big\rceil\ O$$
$$\wedge$$
$$HBr$$

The compound is very easily soluble in water, alcohol, or chloroform, but not in ether. It has no distinct melting point, but turns brown at 138°, blackens at 148° and chars at 153° (uncor.). Irvine, McNicoll and Hynd[1] state that their product softens at 144°, and melts and decomposes at 149–150°.

Tetra-acetylglucosamine Methyl Glucoside.—Eight grams of the compound described above were shaken in a solution of about 175 cc. absolute methyl alcohol with 5.2 grams Kahlbaum's silver carbonate until the solution was halide-free; this required 6–18 hours according to the violence of the shaking. The solution was filtered by suction on a hardened filter, till as free as possible from the extremely fine precipitate of silver salts. About 20 cc. of acetic anhydride were added and the methyl alcohol and acetic anhydride evaporated off on the water bath *in vacuo*. The brown syrupy residue was boiled for half an hour with 20–30 cc. acetic anhydride which was gotten rid of as before. The residue, sometimes sirupy and sometimes crystallin, was taken up with absolute ethyl alcohol and boiled for 20 minutes with bone-black. On filtration the solution was a clear yellow or brown. 15–25 cc. amyl acetate were added and the solution evaporated on the water bath to a thick sirup, or until a heavy precipitate appeared. After standing over night, the sirup solidified and the amyl acetate was filtered off by suction. Occasionally the residue is sticky, of about the consistency of warm molasses candy, and in this case it can be dried on a porous plate, well mixed with 10–15 cc. dry ether and filtered.

If the precipitate is nearly white, it can be freed of the last traces of amyl acetate and acetic anhydride by boiling it a few minutes with ether, filtering and drying *in vacuo* over sulfuric acid and potassium hydroxide. Otherwise the precipitate must be recrystallized again and washed with dry ether.

The substance is a fine white crystallin powder and melts sharply at 150.5° (uncor.). It resolidifies without changing, and melts again at the same point.

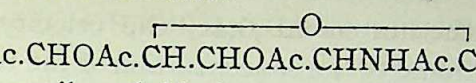
Calculated for $C_{15}H_{22}O_9N$: C, 49.86; H, 6.36; N, 3.88.
Found: C, 50.11; H, 6.53; N, 4.20.

[1] *Loc. cit.*

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This would indicate the structure:



The compound is easily soluble in water, alcohols (methyl, ethyl, isobutyl and isoamyl) and glacial acetic acid; it is difficultly soluble in acetone and warm ether, but practically insoluble in chloroform, the hydrocarbons, and ethyl and amyl acetates.

NEW BOOKS.

Introduction to General Chemistry. By JOHN TAPPAN STODDARD, PH.D. Published by The Macmillan Co., New York, 1910. xviii + 432 pages.

This small text-book of elementary chemistry is intended to be used in connection with lectures or recitation talks and discussions. It contains a concise account of some of the more important facts of descriptive chemistry and of those laws and theories that are usually considered in elementary courses. The order of arranging the elements is somewhat different from that usually followed, in that sulfur and sulfuric acid come immediately after oxygen and hydrogen, and precede the halogens. This is done, as the author states, for the purpose of "placing sulphuric acid in the position which it occupies in actual practice." The periodic law is not mentioned until the last chapter. Quantitative relations receive considerable attention and the student is referred for the details of these experiments to the author's "Quantitative Experiments." The appendix contains a number of useful tables.

Taken as a whole the book is carefully written and when used in connection with a course of lectures and discussions will undoubtedly aid the student in laying a good foundation upon which he can build in more advanced study. EDWARD H. KEISER.

Qualitative Chemical Analysis, Organic and Inorganic. By F. MOLLWO PERKIN, Late Head of the Chemistry Department, Borough Polytechnic Institute, London. Third edition, 337 pages. Published by Longmans, Green & Co.

In the preface the statement is made by the author that in the teaching of chemistry "the theoretical knowledge is generally kept rigidly apart from the facts practically gained, so that the student loses all the mutual help which the two branches of study afford each other," and, that, recognizing this difficulty, he has endeavored "to write a book in which theory and practice are more or less dovetailed." Nevertheless, in the opinion of the reviewer, the author has, in the inorganic part, kept the theory introduced fairly well separated from the practical work. The things which in reality are more or less dovetailed in the book (pp. 25–152) are dry tests, metathetical test-tube reactions, and descriptive chemistry. The theory, given for the most part in the form of dogmatic statements, is largely concentrated in the 13 pages of Chapter II. Mass action is

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introduced with the heterogeneous equilibrium, $CaCO_3 \rightleftarrows CaO + CO_2$, after which follows the statement that "the velocity of the reaction at any instant is proportional to the concentration of the reacting substances." Such a treatment is well calculated to confuse the beginner.

The directions for the detection of lead in the copper group (p. 172) are faulty, and on p. 173 it is stated that the residue left upon boiling the hydrochloric acid precipitate from the yellow ammonium sulfide solution with concentrated hydrochloric acid is As_2S_3 (instead of As_2S_5). The book contains a number of other chemical errors. For example, on p. 28, $AgNH_3^+$ is described as a complex ion derived from NH_4^+ by the substitution of silver for 1 hydrogen atom; the complex is really $[Ag(NH_3)_2]^+$. On p. 32, Hg_2NH_2Cl is "aminomercurous chloride," but on p. 33 it has become "mercurous ammonium chloride;" the black substance really is $NH_2HgCl + Hg$. On p. 246 chloroplatinic acid is called "hydroplatinic acid;" on p. 40, $CuSO_4,4NH_3(=[Cu(NH_3)_4]SO_4)$ is referred to as a copper ammon*ium* compound, and "ferric hydroxide," on p. 73, line 10, becomes, on line 11, the antiquated "ferric hydrate." As a final example of the author's independence in matters of nomenclature and chemical theory, it is stated on p. 79 that with nickel salt solutions "ammonium hydroxide gives a voluminous greenish basic precipitate which is readily soluble in excess, a deep blue solution of a complex nickel ammonium salt $[Ni(NH_3)_6SO_4]$ being formed. *Consequently* in presence of ammon*ium* salts no precipitation takes place." Non-formation of a precipitate here, of course, is due to the repression of the hydroxyl-ion concentration by the common ion of the ammonium salt.

In Part II, the author apparently has sought to devize a scheme of qualitative organic analysis for students who have not previously been trained in organic chemistry nor had a systematic course in organic preparations; but nevertheless, in his summary (p. 314) he admits that "separations can only be carried out by the student having an intimate acquaintance with theoretical as well as with practical chemistry." Here again he seems to have failed of his purpose to dovetail theory with practice, since the former is exceedingly meager as compared with the empirical facts presented, but perhaps this is due to the nature of the subject. The tests depend in the main upon salt formation or color changes, and no attempt is made to substantiate the indications thereby furnished by the preparation, isolation and characterization of derivatives. In the test for nitrogen, p. 202 (2.), the directions are faulty. The fact that no general scheme of separation can be developed for organic substances shows the hopelessness of such a system of qualitative organic analysis.

For the portion of this review dealing with Part II of the book the writer is indebted to the kindness of Dr. C. G. Derick. G. McP. SMITH.

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Die Anlauffarben, eine neue Methode zur Untersuchung Opaker Erze und Erzgemenge. By DR. MAX LEO. pp. 74 and 1 colored plate. Theodor Steinkopff, Dresden, 1911. Price, 2 M.

The study of opaque minerals and metals in polished sections under the microscope has heretofore depended upon the principle that their polished surfaces reflect light with characteristic peculiarities. The method described by Leo depends upon the fact that different substances possessing a metallic luster tarnish differently under the influence of certain reagents and that if the substance be crystallin the same crystal faces will be similarly tarnished, while different faces will exhibit different tarnish colors.

The method is separable into two parts: Certain minerals when polished are affected by decomposing agents in such a way as to yield distinct and characteristic tarnishes that may easily be distinguished under the microscope in reflected light. By comparing the colors on their various surfaces the particles may be oriented and their crystal systems determined. In cases in which characteristic colors are not produced by simple treatment with reagents, the thin polished slice is treated with a reagent while a galvanic current is passed through it. Under these conditions, if the proper reagent be selected, a characteristic tarnish will usually be produced.

The little brochure gives detailed directions for carrying out the tests and concludes with a table containing the author's observations on a number of common minerals. This table records the behavior of polydymite, pyrite, marcasite, linneite, millerite, barnhardtite, pyrrhotite, chalcopyrite, cubanite and bornite under the influence of 13 sets of conditions.

W. S. BAYLEY.

RECENT PUBLICATIONS.

Annales de la science agronomique française et étrangère. Paris: L. Grandeau. 8°, Année 1911 (2 volumes en 6 fascicules). 22 M.

Analyse des Harns. 11 Aufl. von Neubauer-Huppert's Lehrbuch. 1 Hälfte. Wiesbaden: C. W. Kreidel. 8°, 15 M.

ANDÉS, L. E.: **Die Fabrikation der Flaschen- und Siegellacke.** 3 M. **Verarbeitung des Horns, Elfenbeins.** 2 Aufl. 3 M. Wien: A. Hartleben.

BANG, J.: **Chemie und Biochemie der Lipoide.** Wiesbaden: J. F. Bergmann. 8°, 66.5 M.

BARR, J. A.: **Testing for Metallurgical Processes.** San Francisco: Mining and Scientific Press. 12°, 216 pp., $2.00.

BASKERVILLE, C. AND CURTMAN, L. J.: **A Course in Qualitative Chemical Analysis.** Macmillan.

BAYLISS, W. M.: **The Nature of Enzyme Action.** 2nd Ed. Longmanns. 8°, 3s, 6d.

BENRATH, A.: **Chemische Konstitutionsbeweise.** Heidelberg: C. WINTER. 1.20 M.

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BERTEKMANN, W: Lehrbuch der Leuchtgasindustrie. 1. Bd. Stuttgart: F. Enke. 20 M.

BILTZ, H: Introduction to Experimental Inorganic Chemistry. Chapman and Hall. 8°, 5s. 6d.

BROWN, M.: Chemistry of Coal. Published at the Office of "The Science and Art of Mining."

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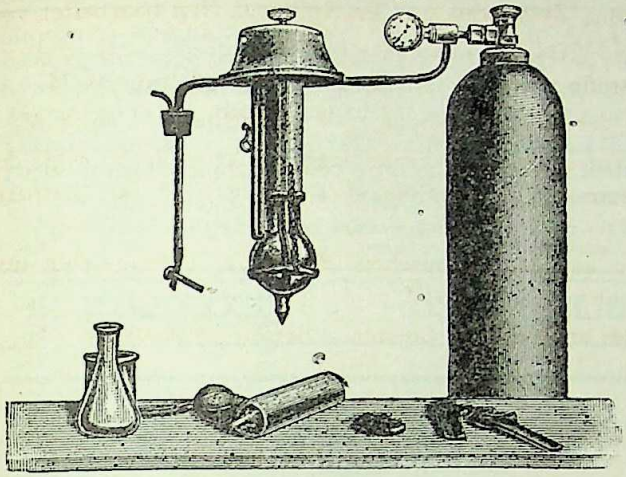
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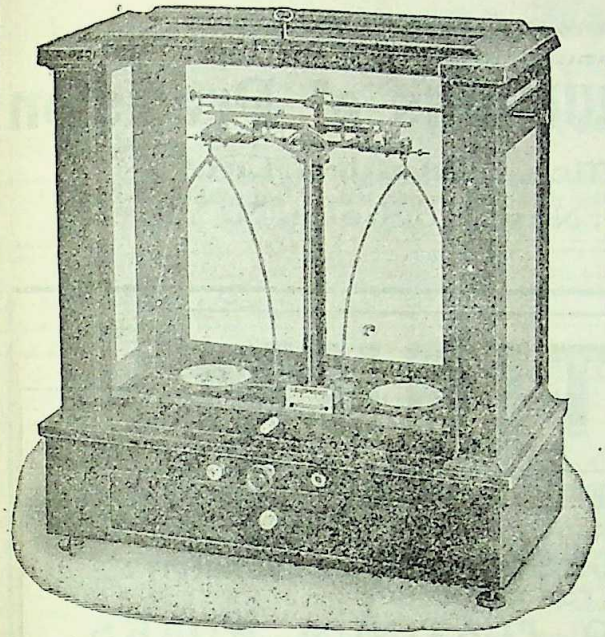
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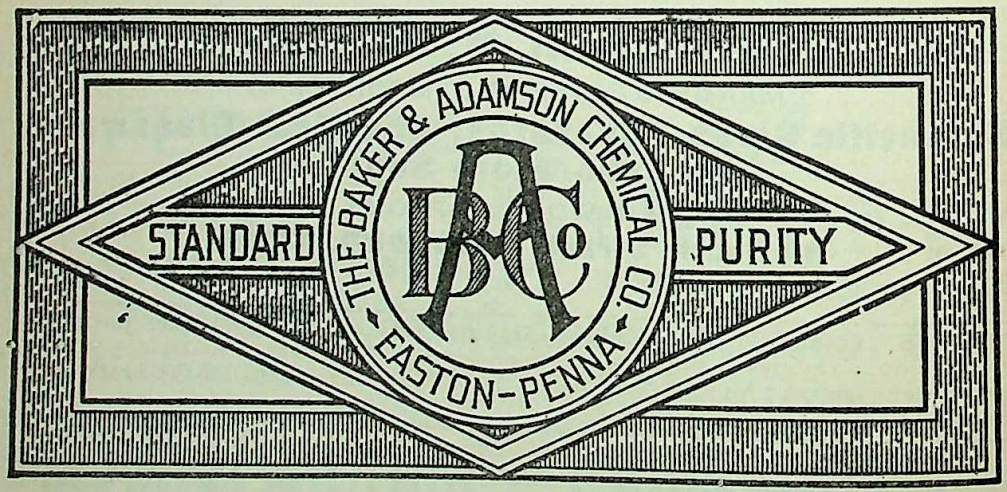
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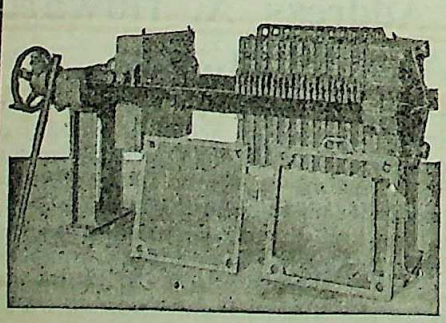
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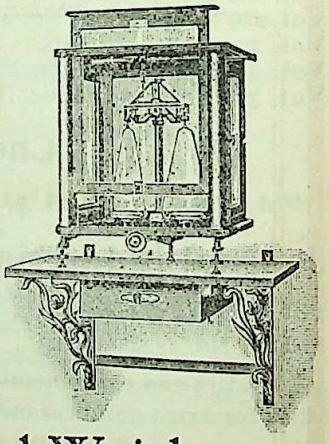
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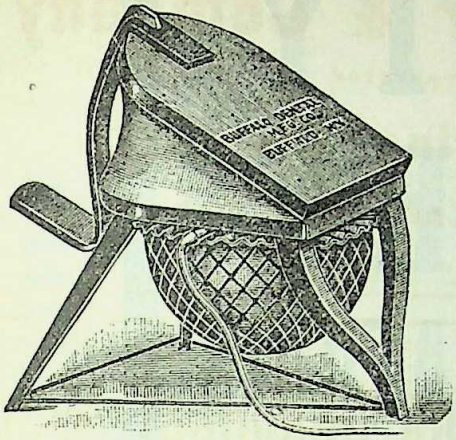
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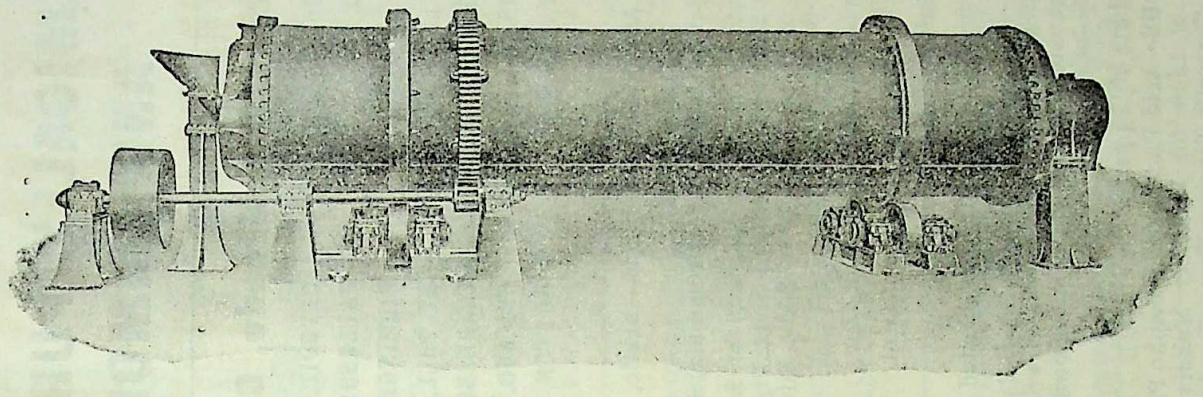
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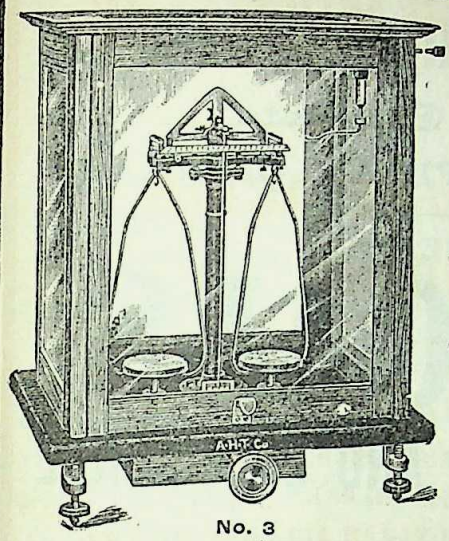
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MEETINGS OF THE SECTIONS.

[Full accounts of meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

NASHVILLE SECTION.

Meetings of the Section have been held in Furman Hall of Vanderbilt University with programs as follows:

February 17, "Salvarsan, or Ehrlich-Hata 606," by Dr. R. W. Balcom. March 17, "The Separation and Detection of Calcium and Strontium by the Sulfite Method," by Dr. J. I. D. Hinds. April 21, "Research Investigations on the Marketing of Poultry," by Mr. H. C. Pierce, Special Agent, Food Research Laboratory, U. S. Bureau of Chemistry.

L. JUNIUS DESHA, *Secretary.*

ST. LOUIS SECTION.

The April meeting was held in connection with the St. Louis Chemical Society on the 10th, at the St. Louis Academy of Science. Mr. H. E. Wiedemann presented a paper on "Calcium Cyanamide," and Mr. Leo R. A. Suppan gave an abstract of the recent work that has been done in organic chemistry.

The May meeting was held on the 8th, at the St. Louis Academy of Science. Mr. H. V. Farr spoke on "Rapid Estimation of Arsenic in Medicinal Drugs." Mr. W. F. Monfort gave an illustrated talk on "The Character of the Mississippi River Water at St. Louis." In this paper Mr. Monfort illustrated his method of depicting water analyses on charts, in terms of chemical equivalents, instead of parts per million. The present secretary of the Section tendered his resignation, which was accepted. Mr. George W. Wallace was then elected to the office.

R. NORRIS SHREVE, *Retiring Secretary.*

INDIANA SECTION.

The Section met in the chemical lecture room of the School of Medicine, Indiana University, Indianapolis, Ind., Friday evening, April 14th. Papers were read on "Proteins, their Classification, Purpose and Digestion Products," by Dr. F. C. Hollis, and on "Determination of Moisture in Coal," by John White.

A. D. THORBURN, *Secretary.*

PHILADELPHIA SECTION.

The April meeting of the Section was held in the Engineers' Club on April 20th after the usual informal dinner. The program was as follows: "A Volumetric Determination of Phosphoric Acid," by J. Rosin.

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An informal symposium on sulfuric acid, in which the following gentlemen took part, discussing some of the features of this interesting subject: "History of the Glover Tower," by Henry Glover, a son of the original inventor of the tower. "The Contact Process," by Dr. Wm. M. Grosvenor, of New York City. "The Wedge Pyrites Burner," by Utley Wedge, the inventor of this burner.

C. S. BRINTON, *Secretary.*

PITTSBURGH SECTION.

The regular April meeting of the Section was held on April 20th in Room 105, Thaw Hall, University of Pittsburgh. Mr. M. G. Lovelace, of the Edgar Thompson Steel Works, addressed the Section on "Color Photography." The address was illustrated by lantern slides.

C. C. VOGT, *Secretary.*

LOUISIANA SECTION.

The forty-ninth meeting was held at the Directors' Room of the Board of Trade, New Orleans, La., Friday, April 21st, at 8 P.M.

An address on "The Cycle of the Elements in Nature," by W. E. Cross, Ph.D., Research Chemist, Louisiana Sugar Experiment Station, was followed by five-minute discussions on chemical topics.

GEO. B. TAYLOR, *Secretary.*

KANSAS CITY SECTION.

The April meeting of the Section was held in the Board of Health rooms at the State House, Topeka, Saturday afternoon, April 22nd, at 3 o'clock. The program was as follows:

"Acidity in Flour and its Relation to Other Constituents," by C. O. Swanson. "The Influence of Certain Chemical Substances on the Baking Quality of Flour," by J. T. Willard. "On Standard Weights and Measures," by Dr. Crumbine. "Nitrates in Drinking Water," by C. C. Young.

E. A. WHITE, *Secretary.*

PUGET SOUND SECTION.

The Section held their regular meeting for the month of April on the evening of the 25th in the rooms of the Seattle Commercial Club.

The meeting was preceded by the regular dinner, after which was held a short business meeting, followed by an open meeting of the Commercial Club which was turned over to our Section. The subject of the evening was "Iron and Steel."

J. H. LINTON, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The following papers were presented at a meeting of the Section on April 26th. "The Determination of Carbon in Iron and Steel," by Dr. Helen Isham. "A New Reagent for Potassium," by Dr. L. L. Burgess and Oliver Kamm. "The Correlation of Ionization and Structure," by C. G. Derick.

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Dr. Alexander Smith, President of the Society, delivered an address on "Vapor and Dissociation Pressures" before a special meeting of the Section on May 6th.

GRINNELL JONES, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club on Thursday evening, April 27th. Dinner at 7 o'clock was followed by an address on "The Preparation of Alizarin," by Prof. J. H. Appleton of Brown University.

ALBERT W. CLAFLIN, *Secretary.*

MINNESOTA SECTION.

The 33rd regular meeting of the Section was held in the Chemical Laboratory of the University of Minnesota, Friday evening, April 28th, with 39 in attendance.

The following papers were presented: "Historical Outline of Food Adulteration and Pure Food Legislation," by Julius Hortvet. "The National Pure Food Law and Methods of its Administration," by A. S. Mitchell.

FRANCIS C. FRARY, *Secretary.*

NORTHEASTERN SECTION.

A special meeting of the Section was held Friday afternoon, April 28th, at 4.15 P.M., in Lowell Building, Massachusetts Institute of Technology, when Professor Svante Arrhenius, of the Nobel Institute, Stockholm, spoke on "The Early Development of the Ionic Theory."

The one hundred and second regular meeting of the Section was held Friday, April 28th, at 8 P.M., at the Twentieth Century Club, Boston, preceded by supper at 6.30 P.M.

Professor Henry Fay, of the Massachusetts Institute of Technology, spoke on "Some Causes of Failures in Metals." Professor Ellwood B. Spear, likewise of the Institute, gave "Some New Observations in Electrolytic Deposition." Mr. Walter A. Patrick, of the Research Laboratory of Applied Chemistry, presented a "Test for Galvanized Iron."

W. K. LEWIS, *Secretary.*

SECTION OF WESTERN NEW YORK.

A meeting of the Section was held at the University, Buffalo, N. Y., Friday, April 28th, with President Watkins in the chair and 43 members and guests present.

Minutes of last general meeting were read and approved. The Nominating Committee proposed the following names to be acted upon at the election of officers at the May meeting. For *President*, W. H. Watkins; *First Vice-President*, A. P. Sy; *Second Vice-President*, J. Klein; *Councillor*, F. A. J. Fitzgerald; *Treasurer*, R. E. Fowler; *Secretary*, Walter Wallace; *Members of Executive Committee*, A. H. Hooker, Alfred Halland, J. F. Schoellkopf, Jr.

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The President then introduced Mr. W. Strohn who gave a paper on "Drying and Evaporating by Vacuum." Discussion followed by Messrs. Hooker, Sy, Watkins, Halland, Shed, Fowler, and Lightfoot, after which the thanks of the Section were tendered to Mr. Strohn for his paper. Meeting then adjourned.

WALTER WALLACE, *Secretary.*

NORTH CAROLINA SECTION.

The spring meeting of the Section was held Friday, April 28th, and Saturday April 29th, at Raleigh.

The following papers were presented: "Neutral Ammonium Citrate Prepared by the Conductivity Method," by R. A. Hall. "The Compounds of Arsenic Halides with Ammonia," by Chas. H. Herty. "The Composition of Solid Phases in Four-Component Systems," by James H. Bell. "The Preparation and Purification of *p*-Bromaniline," by R. A. Hall and W. A. Rudisill. "The Chemical Researches of Ehrlich Leading to '606,'" by R. A. Hall. "The Distribution of Ammonia between Chloroform and Water," by J. M. Bell and A. L. Feild. "What Chemistry has done for the Cottonseed Industry," by James B. Pratt. "A Comparison of the Official Method with the Proposed Modification for the Determination of Crude Fiber," by Hubert Hill. "The Solubility of Iodine in Solutions of Potassium Bromide and of Sodium Bromide at 25°," by J. M. Bell and M. L. Buckley.

BURTON J. RAY, *Secretary.*

CALIFORNIA SECTION.

The fifty-seventh regular meeting of the Section was held on Saturday evening, April 29th, at 8 o'clock, at Bergez & Franks' Café, preceded by the usual dinner. The paper of the evening, "Petroleum Industry of California," was presented by John F. Blowski, of the Union Oil Company.

CHARLES S. ASH, *Secretary.*

WASHINGTON SECTION.

A special Baltimore meeting of the Section was held in Hopkins Hall, Druid Hill, Saturday, April 29th, at 8 P.M.

The program consisted of an address on "General Methods for the Separation of Organic Compounds," by Dr. E. E. Reid.

The 207th meeting was held at the Cosmos Club, Washington, Thursday, May 11th, at 8 P.M.

The following program was presented: "Some Effects of Tropical Sunlight," by R. F. Bacon. "The Catalytic Power of Soils," by M. X. Sullivan. "Melting Points of Minerals in the Light of Recent Investigations on the Gas Thermometer," by R. B. Sosman. "Brief Notes and Exhibition of Apparatus and Specimens."

H. S. BAILEY, *Secretary.*

IOWA SECTION.

The spring meeting of the Section was held in the Chemistry Lecture

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Room of Coe College at Cedar Rapids, Iowa, on Saturday, April 29th, with program as follows: "Illustrative Experiments in the Analysis of City Gas for First-Year Students," by Prof. C. O. Bates, Coe College. "Nitrogen in Rain and Snow," by Dr. Nicholas Knight, Cornell College. "The Commercial Manufacture of Ether," by Dr. L. W. Andrews, Davenport, Ia. "Perchloric Acid in Electro-analysis," by Dr. W. S. Hendrixson, Grinnell College. "Relation of Chemistry to Economic Geology," by Professor G. F. Kay, Department of Geology, State University of Iowa. "The Temperature Coefficients of Fluidity of Aqueous Solutions of Electrolytes," by Dr. J. N. Pearce, State University of Iowa.

The following officers were elected for the ensuing year: *President*, L. W. Andrews; *Vice-President*, C. O. Bates; *Secretary*, J. N. Pearce; *Councilor*, E. W. Rockwood.

J. N. PEARCE, *Secretary*.

MILWAUKEE SECTION.

The Section held a regular meeting on May 2nd, in the Lecture Room of the Public Museum. Dr. O. P. Watts, of the University of Wisconsin, read a paper on "The Industrial Uses of the Electric Furnace," illustrated with lantern slides and many specimens of products of the electric furnace.

BEN L. SALOMON, *Secretary*.

CORNELL SECTION.

The monthly meeting was held Wednesday night, May 3rd, at 8.00 o'clock in Morse Hall. Judge Irvine, of the Law School, spoke on the subject "Expert Testimony."

J. C. ANDREWS, *Secretary*.

NEW YORK SECTION.

The eighth regular meeting of the session of 1910–'11 was held at Rumford Hall on May 5th with Prof. Chas. Baskerville in the chair.

Resolutions were presented on the death of Mr. Bernard G. Amend.

The chairman drew attention to the fact that the day of the meeting marked the centenary of the birth of John W. Draper, and a committee was appointed to consider some fitting memorial celebration.

The following papers were presented: "A Tetracetyl Glucosamine Glucoside," by M. L. Hamlin. "Studies on Amylase. III. Experiments on the Preparation and Properties of Pancreatic Amylase," by H. C. Sherman and M. D. Schlesinger. "The Lactic Acid Ester of Santalol and Other Santalol Compounds," by F. S. Mason. "Electric Tube Furnaces with Calorite Resistors for Laboratory Work," by S. A. Tucker. "A New Rapid Method for the Determination of Manganese in Iron and Steel," by F. J. Metzger and L. E. Marrs. "The Oxidation of Ferrous Salts," by Chas. Baskerville and Reston Stevenson. "Contributions to the Chemistry of Anaesthetics. III. Nitrous Oxide," by Chas. Baskerville and Reston Stevenson.

C. M. JOYCE, *Secretary*.

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CONNECTICUT VALLEY SECTION.

The second meeting of the Section was held in the Chemical Lecture Room at Trinity College, Hartford, at 8.15 P.M., May 6th, with 22 members present. The following officers were elected: *Treasurer*, Mr. A. L. Burwell; *Executive Committee*, Mr. E. B. Hurlburt, Mr. W. S. Rowland and Mr. J. A. Newlands. Two papers were presented: "Accuracy in Certain Difficult Determinations," by Dr. Morley; "Latest Moulded Electrical Insulations," by Mr. Kurt R. Sternberg.

WARREN I. KEELER, *Secretary*.

SECTION OF EASTERN NEW YORK.

The May meeting of the Section was held in the Union College Chapel, Schenectady, on Friday evening, May 12th, at 8 o'clock.

The following paper was presented, illustrated with lantern slides: "The General Subject of Sewage Disposal," by Robert Spurr Weston, Sanitary Expert.

G. R. FONDA, *Secretary*.

Dr. Ellen Henrietta Richards.

The death, after a brief illness, of Dr. Ellen Henrietta Richards has removed one of the best known and highly respected members of the American Chemical Society, and brought to a close a life of unusual activity and far-reaching influence. Soon after her graduation from Vassar College in 1870, Mrs. Richards began her work in Chemistry, in association with Professors John M. Ordway and William R. Nichols, and laid the foundation for the public service which was the dominating feature of her later years. Her contributions to the examination of the inland waters of Massachusetts, undertaken by the State Board of Health in 1887, which has since become a model for other similar undertakings, were of great importance, and her publications in this and other departments of the chemistry of sanitation and of home economics have been numerous and influential.

Always a helpful teacher, whether in her classes in the Massachusetts Institute of Technology or upon the lecture platform, and with a rare gift of leadership and organization, Mrs. Richards devoted herself unsparingly to the service of others, and more especially to the promotion and advancement of the education of women, and to the conservation of human life and human energies. Her activities were so manifold and varied that their protrayal is beyond the scope of any brief words of appreciation, but preparations are already being made to publish an adequate record of her life work.[1] Her high purposes will live in the achievements of the many whom she has incited and inspired to earnest effort in behalf of the causes which were dear to her, but all will sadly miss her encouragement and leadership.

H. P. TALBOT.

[1] A somewhat more extended notice is to be found in *J. Ind. Eng Chem.*, 3, 352.

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THE VAPOR PRESSURES OF MERCURIC CHLORIDE, BROMIDE AND IODIDE.

BY F. M. G. JOHNSON.

Received March 10, 1911.

The measurement of the vapor pressures of mercuric chloride, bromide and iodide has already received the attention of a number of investigators. Faraday appears to have been the first to observe that these salts are volatil at comparatively low temperatures (later contradicted by Riegel[1]) but until a much later date no quantitative measurements were made. The chloride has been studied by Richter[2] and Carnelley,[3] while this salt and the bromide and iodide have been investigated by Arctowski[4] and Wiedemann, Stelzner and Niederschulte,[5] the iodide by Ditte.[6] Dynamic methods chiefly were employed, which at high temperatures are not likely to give reliable results; further, the figures given by these investigators show considerable disagreement in many instances.

The method employed in this work was similar to that used for determining the dissociation pressures of ammonium chloride, etc.[7] A few changes were made in the apparatus and are shown in Fig. 1.

The substance, of which the vapor pressure is to be determined, is placed in the tube at F which, having been evacuated with the mercury pump

[1] *Arch. Pharm.*, 2, 61, 294.
[2] *Ber.*, 19, 1057 (1886).
[3] Melting and Boiling Pt. Tables, (1887).
[4] *Z. anorg. Chem.*, 7, 167 (1894). *Ibid.*, 12, 260 (1903). } Abegg, Handbuch, 2, II, 622.
[5] *Verh. phys. Ges.*, 3, 159 (1905).
[6] *Compt. rend.*, 140, 1162.
[7] *Z. physik. Chem.*, 61, 457 (1908); 65, 36 (1908).

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and sealed, is surrounded by the metal tube shown in the diagram to insure equalization of temperature.

To obtain the zero reading of the spiral at any temperature at zero pressure, air is blown through the tube *A* to cool the substance in *F*. The tube *A* may be removed and replaced by a plug of asbestos when a pressure reading is to be taken. *B* is a cylinder of asbestos closed at the bottom by a plug of asbestos wool. Readings of the spiral at zero pressure were taken before and after each vapor pressure reading. If they differed appreciably, the observations were repeated.

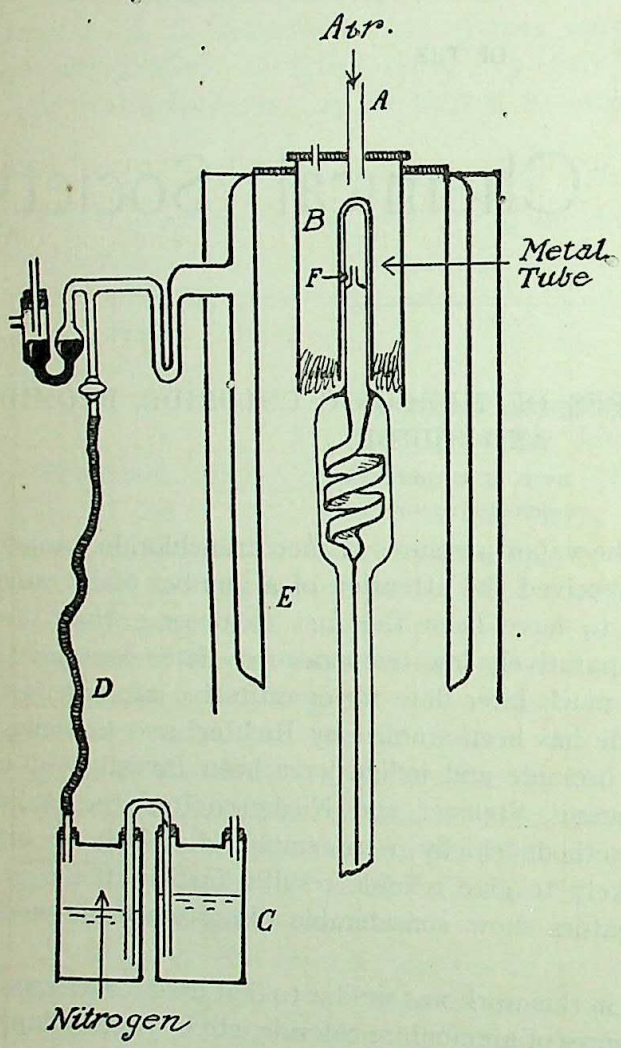


Fig. 1.

The interior of the hollow copper cylinder *E* was connected by means of the rubber tube *D* with a reservoir of nitrogen *C*. This had as its object the prevention of oxidation in the interior of the cylinder, which when air was used became considerable at high temperatures, with consequent inefficiency of the temperature regulation. The spiral used was sensitive to a pressure change of 1 mm. of mercury.

Mercuric Chloride.

The salt used was obtained from Harrington Bros. It was recrystallized several times from its aqueous solution and then sublimed. The following figures were obtained:

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Temp.	Press. in mm. Hg.
152°	3
195	20
231	82
256	198
262	237
275	375
278	421
283	481
302	754

As may be seen from the diagram, Fig. 2, there is a decided break in the curve at 277° corresponding to the melting point as found recently by Jonker.[1] Carnelley[2] gives 287° as the temperature at the melting point. From the curve the boiling point under 760 mm. pressure is 302.5°. The values found by Hittorf, Carnelley, and Freyer and Freyer[2] vary between 302° and 307°.[2]

Mercuric Bromide.

The salt employed was prepared from mercury and bromine in aqueous solution. It was then recrystallized several times, dried and sublimed. The following results were obtained:

Temp.	Press. of mm. Hg.
162°	3
206	29
229	73
233	88
238	106
247	136
255	174
276	293
290	413
306	597
318.5	764

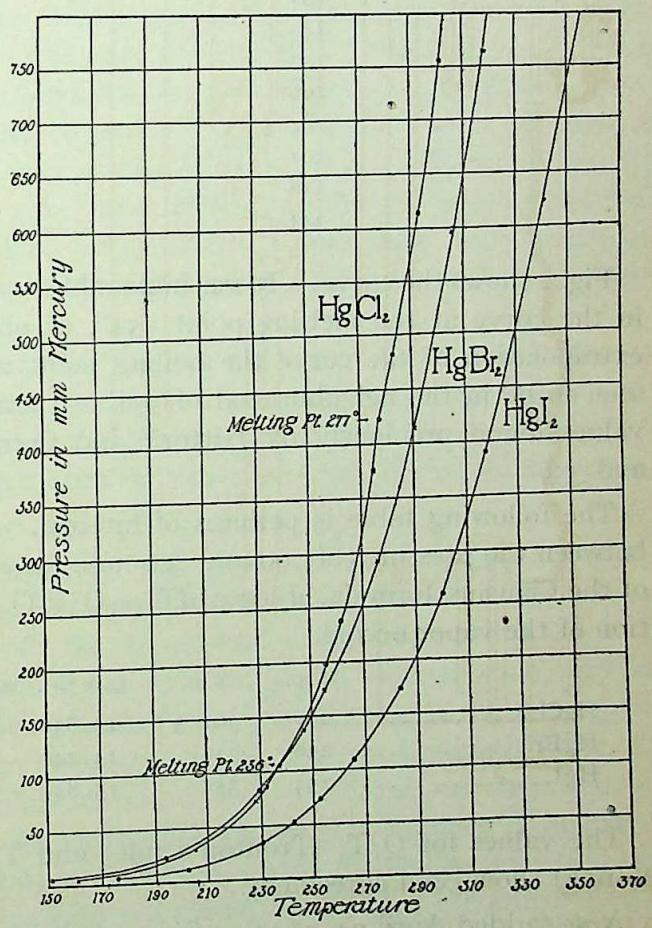


Fig. 2.

The curve obtained is shown in Fig. 2, in which the effect of the melting point is quite evident. The temperature at this point, 236°, agrees with

[1] *Chem. Weekblad*, 6, 1053 (1909).
[2] Landolt and Börnstein, Tabellen.

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that found by Reinders.[1] Other values found previously by Oppenheim[2] and Carnelley[2] vary between 222° and 244°. The curve shows the boiling point under 760 mm. pressure to be 318°. Carnelley and Freyer and Freyer[2] found 319° and 325° respectively.

Mercuric Iodide.

The salt used was prepared from mercuric nitrate and potassium iodide in aqueous solution. It was recrystallized several times from a nitric acid solution, carefully washed, dried and sublimed. The following are the values found:

Temp.	Press. in mm. Hg.
177°	3
203	10
231	32
243.5	51
253	73
266	108
284.5	173
301	260
318	390
341	624

Fig. 2 shows the curve. It was impossible to observe any decided change in the curve at the melting point 254°, as observed by Reinders.[1] By extrapolation of the curve the boiling point under 760 mm. pressure is seen to be in the neighborhood of 351°. Carnelley[2] found 349°. Other values found previously by Hittorf[2] and Carnelley[2] vary between 339° and 359°.

The following table is perhaps of interest. The heats of vaporization between the pressures of 700 and 800 mm. have been calculated by means of the Clausius formula, $d \log p/dT = Q/RT^2$ assuming that no dissociation of the vapor occurs.

	M. p.	B. p.	Q in cal.	Q/T_1 750 mm.	T_1 750 mm./T_2 450 mm.
HgCl.....	277	302.5	14.630	25.44	1.040
HgBr.....	236	318	14.240	24.13	1.043
HgI.....	254	351	15.840	25.47	1.042

The values for Q/T_1 (Trouton's rule) and T_1/T_2 (rule of Ramsay and Young) show good agreement.

Note (added April 24, 1911).—Since this work was completed a paper on "The Vapor Pressures and Molecular Volumes of the Mercuric Halides," by Prideaux,[3] has been published. The method for measuring the vapor pressures consisted in determining the boiling point under

[1] *Z. physik. Chem.*, 32, 494 (1900).
[2] Landolt and Börnstein, Tabellen.
[3] *J. Chem. Soc.*, 97, 2032.

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definit pressures, hence values for the vapor pressures at temperatures below the melting points are not given.

McGILL UNIVERSITY,
MONTREAL.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 67.]

THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE, HYDROCHLORIC ACID AND THEIR MIXTURES.

BY WILLIAM C. BRAY AND FRANKLIN L. HUNT.

Received April 1, 1911.

Introduction.

The object of this investigation was to study, for two salts of widely different conductances, the validity of the present method of calculating the specific conductance of mixtures of salts with a common ion. It has been concluded, from a consideration of existing conductance data,[1] that the degree of ionization of each salt in such a mixture is the same as in a solution of the pure salt at the same total ion concentration. By means of this "ionization rule," and with the additional assumption that the conductances of the ions are constant, values have been calculated for the specific conductances of mixtures which agree well with those determined experimentally.

In any method of calculating the specific conductance L of a binary mixture, this quantity may be divided into two parts, L′ and L″, the *individual specific conductances* of the separate salts, when $L = L' + L''$. Each of these may be calculated by means of a relation of the form:

$$1000\,L' = (C'\gamma')(\Lambda'_k + \Lambda'_a), \qquad (1)$$

where C′ is the concentration, γ' the degree of ionization, $(\Lambda'_k + \Lambda'_a)$ the sum of the equivalent conductances of the ions of one of the salts in the mixture. According to the above rule γ' has the same value as in a solution of the single salt at the same total ion concentration, and has hitherto been calculated by a method of approximation on the assumption that $\Lambda'_k + \Lambda'_a$ is constant and equal to Λ'_0 the conductance of the salt at zero concentration. This assumption is, of course, an uncertain one in any case, and especially when the transference number is known to change with the concentration. For this reason it must be admitted that the values of ion concentrations calculated by the above method may be considerably in error and it will be shown later that this may be the case even when the calculated and measured conductances agree perfectly.

If in the above formula stress is laid on the idea of equivalent conductance, instead of ion concentration $(C'\gamma')$, then we may write:

[1] For references see Sherrill, THIS JOURNAL, 32, 74 (1910); Mackay, *Ibid.*, 33, 308 (1911).

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$$1000\,L' = C'(\gamma' \Lambda'_k + \gamma' \Lambda_a') = C' \Lambda', \qquad (2)$$

where Λ' is the *individual equivalent conductance* of one of the salts in the mixture. The above rule may now be restated as a purely empirical principle: In a mixture of two salts with a common ion, the equivalent conductance of each in the mixture is the same as the equivalent conductance of the pure salt when present alone at the same total ion concentration. Since, moreover, the equivalent conductance of a salt changes only very slowly with its concentration, it is evident that in a given mixture the value of the specific conductance of one salt (L′), and therefore that of the specific conductance of the mixture, (L) must remain almost constant for different values of $\Lambda'_k + \Lambda'_a$, and also even when Λ'_k and Λ'_a are allowed to vary independently. This result will be illustrated later in connection with the discussion of our experimental results.

Whenever in a given series of mixtures, in which the specific conductance of one substance (L′) remains nearly constant, the calculated values of L differ from the experimental, then the absolute differences must tend towards zero as the ratio of the individual conductances L″/L′ becomes very small. The test of the ionization rule by comparing calculated and experimental conductances will evidently cease to be of value when the ratio L″/L′ becomes less than some small number, say 1 : 10 for ordinary experimental conditions, and will in general be most satisfactory when L′ = L″. Since in the case of existing measurements the equivalent conductances of the two separate salts do not differ greatly, equal individual conductances correspond to approximately equal concentrations, and the maximum range of concentrations (which has however not been covered in practice) lies between the ratios 10 : 1 and 1 : 10. In the present instance the method of calculating receives its most severe test when the concentration of the hydrochloric acid is about one-third that of sodium chloride, and the effective range of concentrations lies between approximately 30 : 1 and 1 : 3.

Experimental Details.—The sodium chloride was precipitated from a nearly saturated solution of Kahlbaum's C. P. salt by leading into it washed hydrogen chloride gas. The crystals were collected upon a Büchner funnel, washed with a little water, and ignited in a platinum dish. A stock solution was prepared, and from it nearly all the other solutions were made by diluting weighed amounts to known volumes. This solution was standardized by measuring the conductances of three approximately 0.01 normal solutions prepared in this way, and comparing these values with those of similar solutions made up by weighing out the solid salt. A less reliable preliminary standardization from two gravimetric silver chloride determinations gave a 0.1 per cent. higher normality for the stock solution.

The absence of an appreciable amount of acid in the stock sodium

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chloride solution was proved by experiments with the indicators, methyl orange and para-nitrophenol, from which it was concluded[1] that the concentration of acid was in the neighborhood of 10^{-6} and certainly was not as great as 10^{-5} normal.

The stock hydrochloric acid solution was prepared by dissolving in conductivity water washed hydrogen chloride gas, liberated by dropping concentrated sulfuric acid into pure concentrated hydrochloric acid. The concentration of this solution, as determined from two probably inaccurate gravimetric silver chloride determinations, was 0.2006 mol HCl per 1000 grams solution. A somewhat lower concentration, 0.2004 mol, was obtained by titrating the chloride (after first neutralizing the acid) with a silver nitrate solution which had been standardized against the stock sodium chloride solution by an exactly similar titration. A still lower value 0.2001 was obtained at a later date from two very accurate gravimetric silver chloride determinations made by Dr. W. D. Harkins. The value finally adopted was 0.2003 mol. HCl per 1000 g. solution.

The potassium chloride used in determining cell constants was prepared by twice recrystallizing the C. P. salt from conductivity water.

Many of the solutions used in making the conductance measurements were prepared by weighing out the required amounts of one or both of the stock solutions, and diluting at 25° to a known volume. The remaining solutions were prepared from these by dilution by means of calibrated measuring flasks.

The measurements were made at 25° in a large thermostat, whose temperature remained constant within 0.02°. This temperature was determined by means of a Baudin thermometer which had been certified by the Bureau of Standards at Washington.

The conductivity measurements were made in the usual way with a slide wire bridge of the Kohlrausch roller pattern. The bridge resistances were standardized to an accuracy of about 0.02 per cent. The slide wire was calibrated by the method of Strouhal and Barus, and in addition the middle point of the wire was checked in an independent determination by means of two equal resistances. The heavy copper lead wires had a resistance of 0.05 ohm. This was subtracted from the measured resistance, which was in no case less than 20 ohms. The specific conductance of the water used was determined before making up a solution, and was subtracted from the measured conductance. The value was always between the limits 0.5 and 1.0×10^{-6}.

Two glass cells of the pipet form,[2] with platinized platinum electrodes, were used in making the conductance measurements. Cell A had horizontal circular electrodes 2 cm. in diameter and 5.5 cm. apart; B had

[1] Cf. Salm, *Z. physik. Chem.*, 57, 500 (1906).

[2] This Journal, 31, 732 (1909).

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vertical electrodes 2.5 cm. square, and about 1 cm. apart. The 0.01 normal solutions were measured in both cells, while cell A was used for the more concentrated solutions and B for the more dilute.

The conductance capacities of the cells (*i. e.*, the ratios of specific conductance to measured conductance), which remained constant throughout the investigation, were derived by measuring the conductance of solutions of sodium chloride and of potassium chloride which were 0.01 normal at 25° (1910 atomic weights). The specific conductances 0.0011873 and 0.0014142, respectively, were derived, as explained below, from the corresponding values of Kohlrausch and Maltby at 18° by means of the temperature coefficients given in the following section.

The ratio of the specific conductances at 18° and 25°, L_{25}/L_{18}, was determined for a number of solutions by measuring at each temperature in separate thermostats the conductance of portions of each solution with the same cell on the same day. In this and in the later work each conductance is based on a series of concordant measurements in which two portions of the same solution were used and the solution in the cell was renewed at least three times.

The experimental values of L_{25}/L_{18} are given in Table I in the fifth column. The "final values" in the sixth column were derived by drawing

TABLE I.—RATIO OF SPECIFIC CONDUCTANCES AT 18° AND 25°.

Solution.			Cell used.	Values of L_{25}/L_{18}.		
Substance.	Conc.	Made from		Measured.	Final.	Déguisne.
NaCl	0:1	Stock soln.	A	1.1618		
		Salt	A	1.1615		
		Salt	M	1.1609		
		Salt	M	1.1622	1.1616	..
NaCl	0.05	....	..	..	1.1624	1.1606
NaCl	0.02	Salt	A	1.1631	1.1632	..
NaCl	0.01	Stock soln.	B	1.1636		
		Salt	B	1.1635		
		Salt	A	1.1637		
		Salt	A	1.1635		
		Salt	C	1.1632		
		Salt	M	1.1638	1.1636	1.1620
NaCl	0.005	....	..	..	1.1638	..
NaCl	0.002	Salt	B	1.1639	1.1639	..
NaCl	0.001	Salt	B	1.1644		
		Stock soln.	B	1.1631		
		Stock soln.	B	1.1629	1.1639	1.1630
KCl	0.01	Salt	A	1.1543		
		Salt	B	1.1536		
		Salt	M	1.1535	1.1538	1.1536
HCl	0.05	Stock soln.	A	1.1141		
		Stock soln.	A	1.1134	1.1136	1.1140
		Stock soln.	A	1.1134		

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a smooth curve through the points obtained by plotting the separate values against the concentration. The corresponding values derived from Déguisne's temperature coefficients[1] are given in the last column for comparison. Some results obtained independently by Mr. A. C. Melcher of this laboratory are also included in the table, and are designated by the letter M in the fourth column: The cells A and B were described above. The cell C used in one series of measurements was similar to A.

An inspection of the table shows the striking agreement of our values of L_{25}/L_{18} with those of Mr. Melcher, and also with those of Déguisne for 0.01 *N* KCl and 0.05 *N* HCl. Déguisne's values for NaCl solutions, however, seem to be about 0.1 per cent. too small.

The specific conductances of 0.01 *N* NaCl and KCl solutions at 25°, which were used in determining the cell constants, were then calculated from the values of Kohlrausch and Maltby[2] at 18° as follows:

Specific conductance × 10^3.	NaCl.	KCl.
At 18° of soln. 0.01 *N* at 18° (Kohlrausch at. wts)	1.0195	1.2243
At 18° of soln. 0.01 *N* at 18° (1910 at. wts.)	0.0188	1.2237
At 25° of soln. 0.01 *N* at 18° (1910 at. wts.)	1.1855	1.4120
At 25° of soln. 0.01 *N* at 25° (1910 at. wts.) (assuming the same coefficient of expansion as for pure water)	1.1873	1.4142

Conductance Data.—The values of the equivalent conductance Λ of sodium chloride and of hydrochloric acid solutions are given in Tables II and III. The equivalent conductances are given for round concentrations[3] but the actual concentrations never differed from these by more than a few tenths of a per cent. The concentrations given in the tables are millimols per liter, 1000 C.

In Table II the measured values of Λ_{25} are given in the second column, while the third column contains final values from measurements made independently by Mr. A. C. Melcher. The corresponding values in the fourth column are derived from the data of Kohlrausch and Maltby at 18° and our own values of L_{25}/L_{18}, the corrections for the expansion of the solutions and the change of atomic weights being made as explained above. The values of Λ_{25} finally chosen (column five) were shown to be concordant by plotting the values of $1/\Lambda$ against $(C\Lambda)^{n-1}$ in the usual way.[4] The value of the exponent n which gave a straight line in a given concentration interval gradually increased with decreasing concentration. Between 0.2 and 0.2 *N* n was 1.40, and between 0.05 and 0.001 *N* 1.45. In a similar plot of the data of Kohlrausch and Maltby at 18° the line corresponding to $n = 1.50$ was chosen in extrapolating to zero concentration. The value of Λ_0 corresponding to this line was found

[1] Landolt-Börnstein-Meyerhoffer, Tabellen (1905), p. 744.

[2] *Ibid.*, p. 755.

[3] Noyes and Johnston, THIS JOURNAL, 31, 996 (1909).

[4] This JOURNAL, 31, 735 1010 (1909). Cf. the following article.

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to be 109.0 at 18° and 127.0 at 25°. The corresponding percentage ionizations 100 γ, and equivalent ion concentrations in millimols per liter 1000 γ C, are given in the last two columns of the table.

TABLE II.—CONDUCTANCE AND IONIZATION OF NaCl SOLUTIONS AT 25°.

Conc. 1000 C.	Equiv. cond. Λ at 25°. Measured.	Melcher.	From Λ_{18}(K&M).	Final.	100 γ.	1000 Cγ.
200	101.70	101.7	..	101.7	80.1	160.2
100	106.79					
	106.79					
	106.80	106.8	106.99	106.8	84.1	84.1
50	111.18	111.15	111.36	111.2	87.55	43.78
20	115.86	..	..	..	..	..
	115.84	115.9	115.88	115.9	91.25	18.25
10	118.68[1]					
	118.72[1]					
	118.74	118.7	118.73	118.73	93.5	9.35
5	120.96	121.0	120.88	120.95	95.25	4.762
2	122.99					
	122.94					
	123.06	123.1	122.96	123.0	96.85	1.937
1	124.03					
	124.17					
	124.19	..	124.05	124.1	97.7	0.977
0	..	..	..	127.0	100.0	..

It is evident that our conductance results agree almost exactly with the values obtained independently by Mr. Melcher at all concentrations, and also with those derived from the data of Kohlrausch and Maltby at 18° at all concentrations except 0.05 and 0.1 *N*. In these two cases, moreover, the difference is only about 0.2 per cent.[2]

The conductance results for hydrochloric acid solutions are given in the second column of Table III. The final values given in the third column were shown to be concordant by means of the $1/\Lambda$, $(C\Lambda)^{n-1}$ plot. The error in the case of the 0.001 normal solution corresponds to that observed by other investigators in measuring the conductance of dilute solutions of acid in water.[3] A fairly satisfactory straight line was obtained between the concentrations 0.005 and 0.2 normal with the exponent $n = 1.40$, but, as a result of a comparison with a similar plot of the results of Goodwin and Haskell[3] at 18°, a higher exponent $n = 1.52$ was used in extrapolating to zero concentration. The value $\Lambda_0 = 424$

[1] This value was obtained in three independent measurements.

[2] This 0.2 per cent. difference indicates a real discrepancy between our results and those of Kohlrausch and Maltby, and for this we are unable to offer an explanation. It is worth noting, however, that the method used in obtaining our results in these solutions was identical in every detail with that employed with the 0.02 and 0.01 *N* solutions, in which cases there is no such discrepancy.

[3] Goodwin and Haskell, *Proc. Am. Acad.*, 40, 415 (1904).

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at 25° therefore corresponds to Goodwin and Haskell's value $\Lambda_0 = 380$ at 18°. The percentage ionizations and ion concentrations are given in the last two columns of the table.

TABLE III.—CONDUCTANCE AND IONIZATION OF HCl SOLUTIONS AT 25°.

Conc. 1000 C.	Equivalent conductance. Measured.	Final.	100 γ.	1000 Cγ.
200	380.2	380.2	86.7	179.4
100	390.4	390.4	92.1	92.1
50	398.6			
	398.2			
	398.5[1]	398.4	94.0	47.0
20	406.5	406.7	95.9	19.18
10	411.4			
	411.8	411.6	97.1	9.71
5	415.3			
	415.8	415.3	98.0	4.90
2	418.4	418.6	98.7	1.974
1	419.0(?)	420.4	99.1	0.991
0	..	424.0	100.0	..

The conductance of hydrochloric acid has been measured at 18° by several investigators, and our results may be compared with these at the concentration 0.05 normal by dividing $\Lambda = 398.4$, first by the conductance ratio $L_{25}/L_{18} = 1.1136$ obtained above, and then by the volume ratio 1.00156 to correct for the change in concentration of the solution. The equivalent conductance thus obtained for a 0.05 *N* solution at 18° is 357.2; Goodwin and Haskell found 358.4; interpolation from the results of Noyes and Cooper[2] gives 357.5; an early and probably inaccurate result[3] of Kohlrausch[4] is 360. It is seen that our result agrees with that of Noyes and Cooper and is only 0.3 per cent. less[5] than that of Goodwin and Haskell.

The results obtained with mixtures of sodium chloride and hydrochloric acid are given in Table IV, the number of the experiments in the first column; concentrations in the next three columns, and measured specific conductance (L) in the fifth. The last three columns contain values of L calculated as described below.

[1] This value 398.5 at 0.05 *N* was obtained with a solution prepared by dilution from a more concentrated solution which had been carefully standardized by Dr. W. D. Harkins.

[2] A. A. Noyes, *Car. Pub. Inst.*, 63, 139 (1907); THIS JOURNAL, 30, 388 (1908).

[3] Noyes and Sammet, *Z. physik. Chem.*, 43, 79 (1903).

[4] Kohlrausch, *Leitvermögen* (1898), p. 160.

[5] On account of this discrepancy it is evident that the value $\Lambda = 425$ at 25° corresponds more closely to that of Goodwin and Haskell at 18° than does the value 424 adopted in our calculations.

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TABLE IV.—SPECIFIC CONDUCTANCE OF MIXTURES OF NaCl AND HCl.

Expt. No.	Conc. 1000 C. NaCl.	HCl.	Total.	1000 L. measured.	1000 L calculated. I.	II.	III.
1....	100.0	99.94	199.9	47.25	48.21	48.17	47.35
2....	99.92	49.94	149.9	29.14	29.62	29.60	29.00
3....	99.93	19.98	119.9	18.06	18.31	18.30	17.95
4....	99.91	9.984	109.9	14.36	14.50	14.49	14.28
5....	99.98	4.998	105.0	12.52	12.59	12.60	12.47
6....	99.98	2.006	102.0	11.41	11.45	11.45	11.40
7....	19.98	49.91	69.89	21.75	21.89	21.88	21.71
8....	20.00	19.99	39.99	10.157	10.27	10.26	10.143
9....	19.98	9.988	29.97	6.253	6.307	6.306	6.225
10....	19.98	3.996	23.98	3.889	3.919	3.919	3.876
11....	19.98	1.997	21.98	3.101	3.118	3.118	3.092
12....	20.00	1.000	21.00	2.709	2.721	2.720	2.705
13....	4.995	12.50	17.495	5.651	5.678	5.678	5.648
14....	5.000	4.996	9.996	2.632	2.650	2.650	2.635
15....	4.996	2.697	7.493	1.621	1.630	1.630	1.618
16....	4.997	0.999	5.996	1.011	1.016	1.016	1.009

Calculation of the Specific Conductance of the Mixtures.—The first method of calculation is based on the principle given in the introduction, that the equivalent conductance of each substance in the mixture is the same as in a solution of the pure substance at the same ion concentration. In order to calculate the ion concentration in the mixture (*i. e.*, the concentration of the common ion) definit values were assigned to the conductance of sodium, hydrogen and chloride ions in the mixture, *viz.*: $\Lambda_{Na^+} = 51.2$, $\Lambda_{H^+} = 348.2$, $\Lambda_{Cl^-} = 75.8$, and a method of approximation was used. (The calculated specific conductance, however, will be shown to be practically independent of these numbers.) The degrees of ionization, γ, given in Tables II and III for the single salts were first plotted against ion concentration, Σi. For each mixture the method of approximation consisted in choosing a provisional value of Σi, reading off the corresponding values of γ_{NaCl} and γ_{HCl} from the plot, calculating a new value of $\Sigma i = (C\gamma)_{NaCl} + (C\gamma)_{HCl}$, choosing a new value of Σi (which is usually found to be the correct one), and repeating the calculation until the assumed and calculated values of Σi agreed. The specific conductance,

$$1000\ L = 127.0\ (C\gamma)_{NaCl} + 424.0\ (C\gamma)_{HCl}, \qquad (3)^1$$

was then calculated. This result was also checked by plotting the equivalent conductances given in Table II and III against Σi, reading off the values of the equivalent conductances Λ_{NaCl} and Λ_{HCl} corresponding to the value of Σi, in the mixture and calculating L by means of the equation:

$$1000\ L = C_{NaCl}\ \Lambda_{NaCl} + C_{HCl}\ \Lambda_{HCl}. \qquad (4)^2$$

[1] Compare Equation 1.

[2] Compare Equation 2.

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TABLE V.—CALCULATION OF THE SPECIFIC CONDUCTANCES OF THE MIXTURES I.[1]

1	2	3	4	5	6	7	8	9	10	11	12	13	14
			Ion concs.										
	100 γ.		1,000 Cγ.		Σi	Equiv. cond. in mixt.		Spec. cond. × 1000.			Difference.	Percentage differences.	
No.	NaCl.	HCl.	(Na^+).	(H^+).	(Cl^-).	NaCl.	HCl.	NaCl.	HCl.	1000 L.	1000 δ.	100 δ/L.	100 δ/LHCl.
1	79.7	89.9	79.7	89.8	169.5	101.2	381.1	10.12	38.09	48.21	0.76	1.6	2.0
2	81.63	91.0	81.55	45.45	127.0	103.7	385.7	10.36	19.26	29.62	0.48	1.6	2.5
3	83.05	91.76	82.98	18.32	101.3	105.4	389.1	10.54	7.774	18.31	0.25	1.4	3.2
4	83.54	92.05	83.46	9.19	92.65	106.1	390.3	10.60	3.897	14.50	0.14	1.0	3.6
5	83.81	92.20	83.79	4.61	88.39	106.4	390.9	10.64	1.954	12.59	0.07	0.6	3.6
6	83.96	92.30	83.94	1.852	85.79	106.7	391.4	10.66	0.785	11.45	0.04	0.3	5.1
7	85.64	93.19	17.11	46.51	63.62	108.8	395.1	2.173	19.72	21.89	0.14	0.7	0.7
8	88.50	94.60	17.70	18.91	36.61	112.4	401.0	2.248	8.018	10.27	0.11	1.1	1.4
9	89.70	95.20	17.92	9.51	27.43	113.9	403.7	2.277	4.030	6.307	0.054	0.9	1.3
10	90.57	95.66	18.10	3.823	21.92	115.1	405.6	2.299	1.620	3.919	0.020	0.5	1.2
11	90.80	95.80	18.14	1.913	20.05	115.4	406.2	2.306	0.812	3.118	0.017	0.5	2.1
12	91.10	95.90	18.22	0.959	19.18	115.7	406.7	2.314	0.4067	2.721	0.012	0.4	3.0
13	91.6	96.2	4.58	12.02	16.60	116.4	407.9	0.581	5.098	5.679	0.028	0.5	0.5
14	93.4	97.1	4.67	4.85	9.52	118.6	411.7	0.593	2.057	2.650	0.018	0.7	0.9
15	94.3	97.5	4.71	2.43	7.14	119.6	413.3	0.598	1.032	1.630	0.009	0.6	0.9
16	94.8	97.8	4.74	0.977	5.71	120.4	414.5	0.602	0.414	1.016	0.005	0.5	1.2

[1] The equivalent conductance and degree of ionization of each substance is assumed to depend on the ion concentration alone; $\Lambda_{Na^+} + \Lambda_{Cl^-} = 127.0$, $\Lambda_{H^+} + \Lambda_{Cl^-} = 424.0$.

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The results of these calculations are given in detail in Table V. The percentage ionizations of sodium chloride and of hydrochloric acid are given in the second and third columns, and the corresponding concentrations of the ions Na^+, H^+ and Cl^- in the next three columns. The individual specific conductances calculated for sodium chloride and hydrochloric acid are given in the ninth and tenth columns, and their sum, the calculated specific conductance of the mixture (1000 L), in the eleventh column. The individual equivalent conductances used in checking these calculations are given in the seventh and eighth column. The calculated specific conductances exceed the measured ones by the amounts given in the twelfth column, 1000δ. In the last two columns these differences are expressed as the percentage differences with reference to (1) and calculated specific conductance and (2) the specific conductance of the acid alone.

The calculated specific conductances are always greater than the experimentally determined values, which indicates that the values calculated for one or both of the individual specific conductances are too large. The small percentage deviations from the total specific conductance obtained in some cases (column 13) have little significance, since these deviations necessarily tend towards zero as the ratio of the individual conductances L_{NaCl}/L_{HCl} becomes very large or very small. On the other hand, the rough proportionality between δ and L_{HCl} in the first five experiments (column 14) indicates that the observed deviations are due mainly to errors in the specific conductance of hydrochloric acid. Finally a comparison of the three groups of experiments, Nos. 1–6, 7–12 and 13–16, indicates that the percentage deviations decrease with decreasing ion concentration.

In the second method of calculation, the equivalent conductance of each substance in the mixture was assumed to depend on the total salt concentration, instead of on ion concentration. The equivalent conductance of each substance was plotted against salt concentration, and the individual equivalent conductances corresponding to the total salt concentration in a mixture were read off from this plot. The specific conductance of the mixture was then calculated by means of equation 4. The results are given in Table VI in column 11. The individual equivalent conductances are in columns 7 and 8, and the individual specific conductances in 9 and 10. It is of interest to note that these calculations are much more direct and less time-consuming than those which involve the determination by trial of the total ion concentration.

This method of calculation may be brought into accord with the original "ionization rule" by assuming that hydrochloric acid has the same degree of ionization as sodium chloride at the same concentration. The solutions of the separate substances at equal concentrations must have the same

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TABLE VI.—CALCULATION OF THE SPECIFIC CONDUCTANCES OF THE MIXTURES II.[1]

1	2	3	4	5	6	7	8	9	10	11	12
			Ion concentration.			Individual equiv. cond.		Spec. cond. × 1000.			Difference
No.	100γ.	$\Lambda_{H^+}+\Lambda_{Cl^-}$	(Na^+)	(H^+)	(Cl^-) Σ i.	NaCl.	HCl.	NaCl.	HCl.	1000 L.	1000 δ.
1.....	80.1	474.8	80.1	80.1	160.2	101.7	380.2	10.17	38.00	48.17	0.72
2.....	81.9	469.8	81.8	40.9	122.7	104.0	384.7	10.39	19.21	29.60	0.46
3.....	83.11	466.7	83.05	16.61	99.66	105.5	387.9	10.55	7.75	18.30	0.24
4.....	83.61	465.4	83.53	8.35	91.88	106.2	389.1	10.61	3.885	14.49	0.13
5.....	83.85	464.9	83.83	4.19	88.02	106.5	389.7	10.65	1.947	12.59	0.07
6.....	84.0	464.3	84.0	1.685	85.69	106.7	390.1	10.67	0.783	11.45	0.04
7.....	85.98	459.2	17.18	42.92	60.10	109.2	394.8	2.182	19.70	21.88	0.13
8.....	88.58	452.2	17.72	17.71	35.43	112.5	400.6	2.250	8.008	10.26	0.10
9.....	89.76	449.3	17.93	8.97	26.90	114.0	403.3	2.278	4.028	6.306	0.053
10.....	90.63	447.1	18.11	3.62	21.73	115.1	405.2	2.300	1.619	3.919	0.030
11.....	90.91	446.5	18.16	1.815	19.98	115.5	405.9	2.307	0.8106	3.118	0.017
12.....	91.10	446.0	18.22	0.911	19.13	115.7	406.3	2.314	0.4063	2.720	0.011
13.....	91.72	444.5	4.581	11.47	16.05	116.5	407.7	0.582	5.096	5.678	0.027
14.....	93.49	440.3	4.674	4.671	9.345	118.7	411.6	0.594	2.056	2.650	0.018
15.....	94.28	438.4	4.710	2.354	7.064	119.7	413.3	0.598	1.032	1.630	0.009
16.....	94.83	437.1	4.739	0.947	5.686	120.4	414.5	0.602	0.414	1.016	0.005

[1] The assumptions are (1) the equivalent conductances depend on total salt concentration, or (2) in each mixture $\gamma_{HCl} = \gamma_{NaCl}$; the values of γ and of $(\Lambda_{H^+} + \Lambda_{Cl^-})$ depend on the total ion (or salt) concentration; $\Lambda_{Na^+} = 51.2$ and $\Lambda_{Cl^-} = 75.8$.

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ion concentration, and it is immaterial whether the individual equivalent conductances and degrees of ionization in the mixtures are considered to depend on the ion concentration or on the salt concentration. For the sake of simplicity in the calculations it was assumed that Λ_{Na^+} and Λ_{Cl^-} remained constant, with the same values as before and that Λ_{H^+} increased with increasing salt concentration.[1] The value of $\Lambda_{H^+} + \Lambda_{Cl^-}$ at each concentration was calculated by dividing the observed conductance (Table III) by the degree of ionization of sodium chloride. From a plot against salt concentration the values corresponding to the total salt concentrations in the mixtures were then determined, and are given in column 3 of Table VI. The specific conductance L of each mixture was next calculated as follows: The degree of ionization of sodium chloride was plotted against its concentration, the value $\gamma_{NaCl} = \gamma_{HCl}$ for each mixture corresponding to the total salt concentration was read off from this plot, the ion concentration calculated, and the value of L obtained from the relation $1000\ L = 127\ (C\gamma)_{NaCl} + (\Lambda_{H^+} + \Lambda_{Cl^-})\ (C\gamma)_{HCl}$. These values of L were of course identical with those obtained as described in the preceding paragraph. It is evident that the results would have been the same if any other assumptions had been made with regard to the conductances of the ions. For example, if Λ_{Na^+} increased slightly with increasing concentration in accordance with existing transference data,[2] and Λ_{Cl^-} decreased or remained constant, then somewhat larger values would have been obtained for $\gamma_{NaCl} = \gamma_{HCl}$, and smaller values for $(\Lambda_{H^+} + \Lambda_{Cl^-})$, but the calculated specific conductances would have been exactly the same.

The specific conductances given in this table are seen to be nearly the same as those in Table V. The individual specific conductances of sodium chloride are, it is true, distinctly larger and those of hydrochloric acid smaller than in Table V, but their sums are practically identical. The small differences in the individual specific conductances correspond to the differences in the individual equivalent conductances, not to the differences in the degrees of ionization given in the tables. These results substantiate the conclusion anticipated in the introduction, that when the equivalent conductances in the mixture are assumed to depend on the ion concentration, the value calculated for the specific conductance

[1] That the cation transference number of hydrochloric acid, and therefore the ratio of Λ_{H^+} to Λ_{Cl^-}, increases with the concentration is a well known fact (A. A. Noyes, *Pub. Car. Inst.*, 63, 313; THIS JOURNAL, 25, 167 (1903); 30, 318 (1908)). Lewis and Sargent (THIS JOURNAL, 31, 364 (1909)) in connection with measurements of diffusion potentials between liquids assumed that the degrees of ionization of potassium chloride and hydrochloric acid are equal, and the satisfactory nature of their results furnishes an indication of the correctness of the assumption.

[2] See the summary of transference data by A. A. Noyes and K. G. Falk which will soon be published in THIS JOURNAL.

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of a mixture must be practically independent of the degrees of ionization assumed. Since finally these calculated specific conductances are always too large it follows that the specific conductance of mixtures of sodium chloride and hydrochloric acid cannot be calculated by assuming the equivalent conductances in the mixture to depend on total ion or total salt concentration. The familiar "ionization rule," stated in the first paragraph of this article, evidently does not apply either, as long as the conductances of the ions are assumed to be constant, or to depend on total ion (or salt) concentration.

Whether or not there are other cases which show similar deviations from this rule cannot be decided without a more critical examination of existing data than has been made by us. This we hope will soon be undertaken in this laboratory.

In interpreting conductance data one of the important factors to be considered is the effect of viscosity.[1] In the present instance, however, the effect of viscosity on the calculated values of specific conductance is negligible, since the viscosities of sodium chloride and hydrochloric acid solutions differ but slightly. Thus in 0.2 normal solutions at 25° the viscosities compared with water are 1.0190 and 1.0135 respectively[2] and that of a mixture 0.1 normal with respect to each substance would be about 1.0162.[3] On assuming this value in Expt. 1, and correcting for viscosity, L was calculated to be 0.04810 instead of 0.4817, as given in Table VI. The difference was smaller in the other experiments.

In interpreting our results it has seemed best to seek some simple modification of the ionization rule which will apply in this case. This is not very difficult, since there are two variables which may be arbitrarily chosen, *viz.*: degrees of ionization and conductances of the ions. For the same reason, however, an agreement between calculated and observed conductances, when reached in this way, has little significance, and certainly does not prove the validity of the assumptions.

The following calculations are presented merely as an illustration of one of the possible methods of reaching the desired result. The degrees of ionization of sodium chloride and hydrochloric acid were assumed to be equal in each mixture and to have the same values as given in Table VI. Lower values for the specific conductance of hydrochloric acid were obtained by assuming that the conductance of the hydrogen ion depended on its own concentration, instead of on the total ion concentration. The conductances of sodium and chloride ions were assigned the same values as before. The results of the calculations are given in Table VII. The concentrations of the separate substances given in Table IV are repeated

[1] MacKay, THIS JOURNAL, 33, 308 (1911).
[2] Reyher, *Z. physik. Chem.*, 2, 744 (1888).
[3] Grüneisen, *Wiss. Abh. Phys. Tech. Reichsanstalt*, 4, 239 (1905).

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in this table. The degrees of ionization and ion concentrations are the same as in Table VI.

TABLE VII.—CALCULATION OF THE SPECIFIC CONDUCTANCES OF THE MIXTURE III.[1]

1	2	3	4	5	6	7	8
	Concs. 1000 C.			Spec. cond. × 1000.			Difference.
No.	NaCl.	HCl.	$\Lambda_{H^+} + \Lambda_{Cl^-}$.	NaCl.	HCl.	1000 L.	1000 δ.
1	100.0	99.94	464.2	10.17	38.00	47.35	—0.10
2	99.92	49.94	455.0	10.39	18.61	29.00	—0.14
3	99.93	19.98	445.7	10.55	7.40	17.95	—0.11
4	99.91	9.984	440.2	10.61	3.674	14.28	—0.08
5	99.98	4.998	436.0	10.65	1.827	12.48	—0.05
6	99.98	2.006	432.2	10.67	0.729	11.40	—0.01
7	19.98	49.91	455.0	2.182	19.53	21.71	—0.04
8	20.00	19.99	445.7	2.250	7.893	10.143	—0.014
9	19.98	9.988	440.2	2.278	3.947	6.225	—0.028
10	19.98	3.996	435.0	2.300	1.576	3.876	—0.013
11	20.00	1.997	432.2	2.307	0.785	3.092	—0.009
12	20.00	1.000	430.3	2.314	0.391	2.705	—0.004
13	4.995	12.50	441.9	0.582	5.066	5.648	—0.003
14	5.000	4.996	436.0	0.594	2.038	2.635	—0.003
15	4.996	2.497	433.1	0.598	1.020	1.618	—0.003
16	4.997	0.999	430.3	0.602	0.407	1.009	—0.002

The calculated specific conductances agree much more closely with the experimental than those previously obtained, but are in this case somewhat too small instead of much too large. It is evident that the agreement would have been almost perfect if somewhat larger degrees of ionization had been assumed for hydrochloric acid, corresponding for example to potassium chloride rather than sodium chloride. This is true of course only when the assumption that the conductance of hydrogen ion depends upon its actual concentration is true, and other assumptions would lead to other values for the degrees of ionization of the acid. Different results would also be obtained if the conductances of sodium and chloride ions were allowed to vary with the concentration. Additional calculations have accordingly not seemed worth while at the present time, since no additional conclusions could be drawn from them.

Summary.

Measurements have been made at 25° of the conductance of 0.001 to 0.2 normal solutions of sodium chloride and of hydrochloric acid and of mixtures of them in which the concentrations were varied systematically.

The specific conductances of the mixtures have been calculated by

[1] γ_{NaCl} and Λ_{HCl} are equal in each mixture and depend on the total ion (or salt) concentration. $(\Lambda_{H^+} + \Lambda_{Cl^-})$ depends on the concentration of the acid in the mixture. $\Lambda_{Na^+} = 51.2$, $\Lambda_{Cl^-} = 75.8$

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means of the familiar ionization rule for mixtures of salts with a common ion, *viz.*: that the degree of ionization of each salt in the mixture is the same as that of a solution of the pure salt at the same ion concentration.

It is shown that large variations in the degrees of ionization (which correspond to different assumptions with regard to the values of the ionic conductances and their change with concentration) produce practically no change in the calculated specific conductances, provided that the conductance of each ion is assumed to depend upon the total equivalent ion concentration. This assumption is identical with stating the equivalent conductance of each salt in a mixture to be equal to the equivalent conductance of a solution of the pure salt at the same ion concentration. The assumption usually made that ionic conductances are constant is included in this more general case.

In the present instance the specific conductances calculated in this way are always greater than the experimental values. The difference is about 1.6 per cent. of the actual specific conductance when the concentration of each substance is 0.1 normal in the mixture, and is less at smaller concentrations. The suggestion is made that the conductance of an ion may depend upon its actual concentration rather than upon the total ion concentration, and it is shown to be possible to obtain a satisfactory agreement between the measured and calculated values by assuming that this is true for hydrogen ion and that hydrochloric acid is ionized to about the same extent as potassium chloride.

The ratio of the specific conductances at 25° and 18° has also been determined for 0.01 normal potassium chloride, 0.05 normal hydrochloric acid, and a number of sodium chloride solutions. Déguisne's results are confirmed for the first two solutions, but seem to be about 0.15 per cent. too low in the case of the sodium chloride solutions.

This investigation and the following one were carried out with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington. It is desired to express here grateful acknowledgment of this financial aid.

BOSTON, March, 1911.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 68.]

THE CONDUCTANCE AND IONIZATION OF CERTAIN SALTS AT 18° AND 25°.

BY FRANKLIN L. HUNT.

Received April 1, 1911.

This investigation is a continuation of earlier work[1] in this laboratory,

[1] A. A. Noyes, *et al.*, *Pub. Car. Inst.*, 63 (1907); THIS JOURNAL, 30, 335–53 (1908); A. A. Noyes and J. Johnston, THIS JOURNAL, 31, 987, 1010 (1909).

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in which it was shown by means of conductance measurements that the empirical dilution law,

$$\frac{(\text{Ion concentration})^n}{(\text{Concentration of un-ionized salt})} = \text{constant, where } n = 1.4\text{–}1.6,$$

holds closely for dilute aqueous solutions of salts of different types over a very wide temperature range. In the present measurements the following substances were investigated at 18° and 25°: potassium and barium bromates, silver and thallium sulfates, magnesium nitrate, lead chloride, and sulfuric acid. Measurements were also made at 0° in the case of sulfuric acid.[1]

The immediate purpose of the investigation was to obtain at 25° accurate conductance data to assist in interpreting the results of solubility and other investigations in this laboratory. The measurements were also made at 18° in order to enable more definit values to be derived for the conductances of the ions. Absolute values of the latter cannot be determined, since they depend upon Λ_0 values obtained from conductance measurements by extrapolating to zero concentration, but an effort has been made to obtain values at 18° and 25° which are consistent with those derived by Kohlrausch at 18° from his careful investigations with dilute solutions.

The measurements at 18° and 25° were made exactly as described in the preceding article, except that the resistance of the lead wires was only 0.02 ohm, instead of 0.05. The measurements at 0° were made in a heavily jacketed cylindrical copper vessel of 18 liters capacity containing a mixture of finely cracked ice and water, in which the conductivity vessel was completely submerged. A powerful stirrer was placed near one side of the thermostat and was protected from the ice by a coarse-mesh wire gauze. By occasionally adding cracked ice, the temperature was maintained at 0° within less than 0.01°. The conductance capacities of the cells were assumed the same at 0°, 18° and 25° and were determined at 18° by means of 0.01 normal potassium chloride solutions, usually before and after the measurements on each salt. They were found to remain constant within less than 0.1 per cent. except during the silver sulfate measurements, where an increase of 0.1 per cent. in the high resistance cell and of 0.35 per cent. in the low resistance cell was detected. Since intermediate values were found when the silver sulfate measurements were about half completed, the conductance capacities were assumed to change at a uniform rate during these measurements.

The substances used (except thallous sulfate and sulfuric acid) were purified by Dr. W. D. Harkins in connection with his work in this laboratory on the effect of salts on the solubility of uni-bivalent salts. Since

[1] The results for sulfuric acid solutions have already been interpreted in an article by A. A. Noyes and M. A. Stewart, THIS JOURNAL, 32, 1139 (1910).

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the details will soon be published in his article, it is sufficient to state at the present time that special precautions were taken to obtain pure materials. The final crystallization was always made from conductivity water. The silver sulfate was carefully prepared and recrystallized in the dark and remained white on shaking with water. The thallous sulfate was a sample purified by recrystallization by Dr. K. G. Falk,[1] of this laboratory. The sulfuric acid was taken from a fresh bottle of Baker and Adamson's "strictly chemically pure" acid, another bottle of which had formerly been carefully tested by Mr. Y. Kato in this laboratory.[2]

A stock solution of each substance was prepared, and from it by dilution was derived a complete series of solutions whose concentrations corresponded very closely to the round concentrations given in the tables below. The results obtained with these solutions were checked by independent measurements, as shown in the tables. In the case of silver sulfate and magnesium nitrate a second stock solution was made up from a second sample of salt prepared by a different method. In the second series of measurements with thallous sulfate and the third with silver sulfate the separate solutions were prepared by weighing out the proper amount of the solid salt. The thallous sulfate was dried at 150–160°, and the silver sulfate at about 100°. The latter salt darkened slightly on heating at this temperature, but no corresponding change in the conductance of the solutions was detected. The check measurements with sulfuric acid were made with two sets of solutions derived from the original stock solution.

These check measurements agreed within 0.1 per cent., except in three instances, 0.2 *N* Tl_2SO_4, 0.002 *N* $Mg(NO_3)_2$ and 0.01 *N* H_2SO_4, where the two values differed by less than 0.2 per cent., and in the dilute silver sulfate solutions, where the results were less satisfactory than in the other cases, doubtless on account of the uncertainty introduced by the variation of the conductance capacity of the low resistance cell. Here the extreme variations were less than 0.3 per cent. in the most dilute solution and less than 0.2 per cent. in the other cases. In the case of thallous sulfate, to test for a possible change of conductance on standing, an approximately 0.02 normal solution was prepared, transferred at once to the conductivity vessel, and measured at intervals of five minutes for an hour and a half. No appreciable change was detected in this case, nor in other dilute solutions on standing several days. Since these measurements were made, Mr. Winninghoff has found in three separate 0.1 *N* solutions a small increase of conductance on standing of not more than 0.2 per cent. His values after 2 to 4 days agreed within less than 0.1 per cent. with that (96.0) given in Table III below. The conductances of the saturated

[1] This Journal, 32, 1557 (1910).

[2] A. A. Noyes, *Pub. Car. Inst.*, 63, 242 (1907).

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solutions of silver sulfate, barium bromate, and lead chloride at 25° were also measured and, as will be shown below, furnish checks for the results obtained in the more concentrated solutions of the regular series. Check measurements in the case of potassium bromate seemed unnecessary, since no serious irregularities were found in the other cases.

Measurements were also made with supersaturated solutions of silver sulfate at 25°. Solutions nearly saturated at 50° and 70° were prepared free from crystals, and cooled to 25°. After the removal of portions for analysis, the solutions were carefully transferred to the conductivity cell, and measurements were made as quickly as possible. The conductance usually remained constant for a few minutes, and then began to decrease steadily. This decrease was undoubtedly due to crystallization on the electrodes, since after the measurements a fine deposit of crystals was generally observed on the electrodes. The initial values obtained in five experiments are included in Table III below.

The most concentrated solutions of thallous sulfate (0.2 normal) and of barium bromate (0.04 normal) were slightly supersaturated at 18°, and crystallization on the electrodes sometimes took place. There was no difficulty, however, in obtaining reproducible values.

Some of the solutions of thallous sulfate and magnesium nitrate were shown to be neutral by means of indicators.[1] They reacted alkaline towards litmus and acid to rosolic acid, thus proving that the concentration of hydrogen ion was approximately 10^{-7}.

The concentrations of the saturated, supersaturated, and stock solutions were determined by direct analysis. Except in the case of thallous sulfate and of sulfuric acid the analyses were made by Dr. W. D. Harkins by methods which will be described in detail in his article. The silver sulfate and lead chloride solutions were analyzed by weighing silver chloride. The two stock solutions of the silver sulfate had been prepared by weighing out salt from which the water had been almost completely removed in a vacuum desiccator at room temperature; the concentrations calculated from these weights differed by 0.1 and 0.2 per cent. from the analytically determined values. The barium and potassium bromate solutions were analyzed by reducing the bromate with hydrazine, and weighing silver bromide. The concentrations of the two magnesium nitrate stock solutions were determined by evaporating known weights of the solutions with sulfuric acid on a water bath, heating, and weighing the magnesium sulfate. The thallous sulfate solutions were prepared by weighing directly salt which had been dried at 150–160°. A single analysis of the stock solution, made by Dr. K. G. Falk, in which the thallium was weighed as iodide,[2] gave a concentration only 0.07 per cent. less than the accepted

[1] Salm, *Z. physik. Chem.*, 57, 471 (1906).

[2] K. G. Falk, THIS JOURNAL, 32, 1560 (1910).

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value. The stock sulfuric acid solution was analyzed by titrating weighed portions (with phenolphthalein as indicator) against carbon dioxide-free alkali, which had been standardized by means of the standard hydrochloric acid solution described in the preceding article.

Concentrations are expressed in equivalents per liter, based on the international atomic weights for 1910. Two-gram equivalents of each of the uni-bivalent salts, including barium bromate, are of course equal to one gram molecule. In the tables given below concentrations are expressed, for convenience, as millimols per liter, 1000 C, at the temperatures in question. During the investigation all dilutions were made at 25° with flasks calibrated at 25°, and concentrations were therefore expressed as mols per liter at this temperature. The concentrations at other temperatures were computed by assuming the temperature coefficient of contraction to be the same as that of water, except in the case of 0.2 normal sulfuric acid. The concentration of this solution at 0° was assumed to be 0.37 per cent.[1] greater than at 25°, instead of 0.28 per cent. as in the other cases.

In the tables round concentrations are given instead of the actual ones. The equivalent conductances (Λ) were derived from the values at the actual concentrations by applying a small correction based on the rate at which Λ changes with C at that particular concentration, as derived from the plots described in the following paragraph. The round concentrations differed from the actual by about 3 per cent. in the case of barium bromate, by only 0.4 to 0.8 per cent. in the case of lead chloride, and by even smaller amounts in the remaining cases.

It is easily shown[2] that when the empirical dilution law given in the first lines of this article holds over a definit range of concentration for some value of n, a straight-line plot must be obtained in the same range on plotting $1/\Lambda$ against $(C\Lambda)^{n-1}$. Conversely, by plotting the results for several values of n, that value which gives the best straight line in a given concentration range may be chosen. In order to compare the curvature of the various lines more easily the values of $(C\Lambda)^{n-1}$ for each n are usually multiplied by a factor such that all the lines pass through a point corresponding to a concentration of say 0.1 equivalent per liter. This method of plotting has proved of great value in interpolating values of Λ at different concentrations, and has also been used in extrapolating to zero concentration to obtain Λ_0 values. In the latter case, however, the results are not very definit, since the values of n to use in extrapolating cannot be accurately determined.

The present results were plotted in this way, and the plots for each salt

[1] Landolt-Börnstein-Meyerhoffer, Tabellen, 326.

[2] A. A. Noyes, *Pub. Car. Inst.*, 63, 50, 334; cf. also THIS JOURNAL, 31, 745, 994, 996, 1010.

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were found to be almost exactly similar at 18° and 25°. Smooth curves were obtained in each case, thus showing that the results at the different concentrations are concordant, probably within 0.1 per cent. The data for the saturated solutions of silver sulfate, barium bromate, and lead chloride at 25° were perfectly concordant with the results at lower concentrations, since the curves obtained at lower concentrations, when produced, passed through the points corresponding to the saturated solutions. The two sets of values are completely independent, and this result therefore furnishes a proof of the accuracy of the conductance measurements. The values for three of the supersaturated solutions of silver sulfate were also concordant with these results, but the two other values (at 0.0718 normal) were not, and were therefore rejected.

By means of these $1/\Lambda$, $(C\Lambda)^{n-1}$ curves it was easy to choose with an accuracy of about ± 0.03 the value of n which gave the best straight line over any given range of concentration. In almost every case there was distinct evidence that the "best" values of n increased with decreasing concentration.[1] Probable values of Λ_0 for each salt were accordingly calculated at 18° and 25° by choosing the best value of n in dilute solutions. These preliminary values were then compared by Dr. K. G. Falk and Dr. W. C. Bray with similar values for other salts at these temperatures, and a concordant series of ionic conductances was finally adopted by them based chiefly on the results of Kohlrausch and his assistants at 18°. The resulting values of Λ_0 for the salts investigated by me are given in the following table, together with the values of n which enable these values of Λ_0 to be obtained by extrapolation (n_0), and approximate values of n between the concentrations 0.02 and 0.1 normal ($n_{0.02\text{-}0.10}$).

TABLE I.—VALUES OF Λ_0 AND n.

Salt.	Λ_0 at 18°.	Λ at 25°.	n_0.	$n_{0.02\text{-}0.10}$.
$KBrO_3$	112.1	129.6	1.53	1.45
$Mg(NO_3)_2$	107.7	125.6	1.45	1.35
$Ba(BrO_3)_2$	103.0	120.0	1.50	1.45
Ag_2SO_4	122.5	143.4	1.58	1.50
Tl_2SO_4	134.4	156.0	1.58	1.50
$PbCl_2$	126.3	147.0	1.65	1.70

The "probable" Λ_0 values derived for the separate salts agreed very well with the final values except in the case of lead chloride. Here the first values (based on the exponent $n_0 = 1.70$) were about one unit less than those adopted as a result of a comparison with the data of Kohlrausch and Grüneisen for lead nitrate and potassium chloride at 18°. It is by no means certain that the larger values are more nearly correct, but they have been adopted for the sake of uniformity with the other results at 18°. It is not improbable, moreover, that our present Λ_0 values are

[1] Cf. THIS JOURNAL, 31, 746, 1011.

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all too high, especially in the case of polyvalent salts, since the exponent n may continue to increase in very dilute solutions, instead of remaining constant as assumed in the extrapolation.

In this table the uni-bivalent salts are arranged in the order of the increasing values of n_o. A comparison with the values of the degrees of ionization given below shows that at any concentration the degrees of ionization decrease in the same order. It is interesting to note that in the case of lead chloride the value of n is usually high throughout and that this salt is less ionized than the other uni-bivalent salts.

The values adopted for the equivalent conductances of the ions are given in the following table:

TABLE II.—EQUIVALENT CONDUCTANCES OF THE IONS.

Cation.	$\Lambda_{18°}$.	$\Lambda_{25°}$.	Anion.	$\Lambda_{18°}$.	$\Lambda_{25°}$.
K^+	64.5	74.8	BrO_3	47.6	54.8
Ag^+	54.0	63.4	NO_3	61.8	70.6
$\frac{1}{2}Mg^{++}$	45.9	55.0	Cl	65.5	75.8
$\frac{1}{2}Ba^{++}$	55.4	65.2	$\frac{1}{2}SO_4$	68.5	80.0
$\frac{1}{2}Pb^{++}$	60.8	71.2	..	..	..
$\frac{1}{2}Tl^{++}$	65.9	76.0	..	..	..

In Table III the values of equivalent conductance (Λ) at different concentrations (1000 C) are given. Saturated solutions are designated by the letter (s), supersaturated by (ss). The value for the saturated solution of barium bromate was determined by Dr. W. D. Harkins. The conductance of the 0.1 normal H_2SO_4 solution was also measured at 18° and found to be 233.2. This agrees within 0.05 per cent. with the result given by Eastman[1] and is 3.6 per cent. greater than that given by Kohlrausch.[2]

The percentage ionizations of the salts ($100\gamma = 100\,\Lambda/\Lambda_o$) are given in Table IV. The degree of ionization of each salt at 25° is seen to be

TABLE III.—CONDUCTANCE DATA.

Conc. at $t°$.	Tl_2SO_4.		$Mg(NO_3)_2$.		$KBrO_3$.		H_2SO_4.	
	18°.	25°.	18°.	25°.	18°.	25°.	0°.	25°.
0	134.4	156.0	107.7	125.6	112.1	129.6	..	..
1	127.35*	147.8*	120.6*	119.5*	109.9	126.9	..	..
2	124.2*	144.2*	100.8*	117.4*	108.7	125.6	..	..
5	118.4*	137.3*	97.7*	113.7*	106.9	123.4	..	..
10	112.3*	130.0*	94.65*	110.05*	104.7	121.0	226.4*	336.8*
20	104.55	120.9	90.9	105.7	102.0	117.8	..	..
25	..	..	..	..	..	116.6	206.95	299.3
50	92.7*	107.1*	85.3	99.0	97.3	112.4	191.5	273.1
100	83.1	96.0	80.5*	93.4*	93.0	107.2	177.2*	251.2*
200	73.8*	85.0*	75.3	87.3	87.8	101.1	165.4	234.7

[1] A. A. Noyes, *et al.*, *Pub. Car. Inst.*, 63, 262 (1907).
[2] Landolt-Börnstein-Meyerhoffer, Tabellen, 746.
* Mean of two values.

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TABLE III (*Continued*).

Conc. at $t°$.	Ag_2SO_4.		$Ba(BrO_3)_2$.		$PbCl_2$.	
	18°.	25°.	18°.	25°.	18°.	25°.
0	122.5	143.4	103.0	120.0	126.3	147.0
1	116.3†	135.7†	97.5	113.6	119.15	138.7
2	113.6†	132.6†	95.5	111.2	115.8	134.5
4	109.85	128.0	..	..	..	..
5	108.4†	126.3†	91.9	106.95	109.2	126.8
10	102.9†	119.9†	88.2	102.7	102.1	118.2
20	96.1*	111.7*	83.6	97.3	93.2	107.6
40	88.0*	102.2*	78.3	91.1	..	..
40.2 (s)	..	..	..	91.1	..	..
50	..	97.7†	..	..	79.2	91.3
53.74 (s)	..	94.3*	..	..	..	..
71.8 (ss)	..	93.5	..	..	..	..
72.0 (ss)	..	92.15*	..	..	..	..
78.2 (ss)	..	..	..	..	..	..
77.54 (s)	..	..	..	..	..	82.6*

somewhat less than at 18°, but the difference decreases with decreasing concentration, and is in general almost negligible in very dilute solutions. It is of interest to note that γ is practically the same for magnesium nitrate

TABLE IV.—PERCENTAGE IONIZATION OF THE SALTS.

Concentration at $t°$.	Tl_2SO_4.		$Mg(NO_3)_2$.		$KBrO_3$.	
	18°.	25°.	18°.	25°.	18°.	25°.
0	100	100	100	100	100	100
1	94.7	94.7	95.3	95.2	98.0	97.9
2	92.4	92.4	93.6	93.5	97.0	96.9
5	88.1	88.0	90.7	90.5	95.3	95.2
10	83.5	83.4	87.9	87.6	93.4	93.4
20	77.8	77.5	84.4	84.1	91.0	90.9
50	69.0	68.7	79.2	78.8	86.8	86.7
100	61.9	61.5	74.8	74.4	82.9	82.7
200	54.9	54.5	69.9	69.4	78.3	78.0

Concentration at $t°$.	Ag_2SO_4.		$Ba(BrO_3)_2$.		$PbCl_2$.	
	18°.	25°.	18°.	25°.	18°.	25°.
0	100	100	100	100	100	100
1	95.0	94.7	94.7	94.7	94.3	94.3
2	92.7	92.5	92.7	92.7	91.7	91.5
4	89.5	89.3	..	..	..	..
5	88.5	88.1	89.2	89.2	86.5	86.3
10	84.0	83.6	85.7	85.6	80.8	80.4
20	78.4	77.9	81.2	81.1	73.8	73.2
40	71.8	71.3	76.0	75.9	..	..
50	..	..	..	..	62.7	62.1
53.74	..	68.1	..	..	..	..
78.2	..	64.3	..	..	..	..
77.54	..	..	..	..	..	56.2

*Mean of two values.
†Mean of three values.

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and magnesium chloride, and for potassium bromate and potassium nitrate. It is slightly less for barium bromate than for barium nitrate, and for thallous sulfate than for silver sulfate. Thallous and silver sulfates are somewhat less ionized than lead nitrate, and all three are much less ionized than nearly all other uni-bivalent salts. In fact below 0.05 normal their degrees of ionization are less than for the two uni-trivalent salts, lanthanum nitrate and potassium citrate, investigated by Noyes and Johnston.[1] The ionization is even less in the case of lead chloride and is still less in the case of cadmium chloride. It is evident that a number of salts[2] such as those of silver, thallium, lead and cadmium, are less ionized than typical salts of the same valence product type[3] and thus occupy an intermediate position between typical strong electrolytes, and weak electrolytes, such as mercuric chloride.

In conclusion the author wishes to express his indebtedness to Professor A. A. Noyes and Professor W. C. Bray, of this laboratory, for assistance in connection with the experimental work and the preparation of this article for publication.

BOSTON, March, 1911.

CONTRIBUTIONS TO THE ELECTROCHEMISTRY OF HYDRONITRIC ACID AND ITS SALTS. I. THE CORROSION OF SOME METALS IN SODIUM TRINITRIDE SOLUTION.

BY J. W. TURRENTINE.

Received March 10, 1911.

Introduction.

While hydronitric acid has received its full quota of attention from investigators in both inorganic and organic chemistry, and a large mass of experimental data concerning this interesting new addition to the family of inorganic acids has been accumulated, its study from the electrochemical point of attack has been for the most part neglected.

It is the purpose of the research, one chapter of which is here reported, to investigate the behavior of the nitride ion (1) on being discharged against a soluble anode; (2) on being discharged against an insoluble anode; (3) on being acted upon in the anode region by discharged anions, or anode products (electrochemical oxidation); and (4) on being acted upon in the cathode region by discharged cations, or cathode products (electrochemical reduction). Also, the determination of some of the electrochemical constants of hydronitric acid and its compounds is anticipated. In all of this work special attention will be paid to a comparison of the behavior of the nitride ion with that of other ions, in order that its true position in the family of anions may be shown.

[1] THIS JOURNAL, 31, 1002 (1909).

[2] Cf. Abbott and Bray, THIS JOURNAL, 31, 753 (1909).

[3] Noyes and Johnston, *Loc. cit.*, 1003.

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The anion from hydronitric acid and its salts, the trinitrides, would be called the *trinitride* ion. However, as there is no other series of water-soluble nitrides capable of forming anions containing nitrogen alone, no confusion can arise if this name be abbreviated to *nitride* ion. So, in this paper, the N_3^- ion will be so designated. Dennis and Browne[1] have applied the name *nitrine* to the hypothetical polymer, $(N_3)_2$, to connote the predicted analogy of that substance with the free halogens. Likewise, the name, nitride ion, connotes the analogy of this ion with the ions from the halogenides, the cyanides and with other oxygen-free anions.

The existence of analogies between the nitride and chloride ions[2] has been frequently intimated. Evidences gathered from the corrosion by the nitride ion, and its oxidation and reduction electrochemically, will be brought to bear on this interesting comparison.

Historical.—Ostwald[3] applied conductivity methods to the determination of the degree of ionization of hydronitric acid in aqueous solution, in order to determin its relative strength as an acid. West[4] repeated Ostwald's work, and Hantzsch[5] performed experiments of like nature. Hittorf[6] electrolyzed ammonium trinitride in aqueous solution, obtaining hydrogen and nitrogen as the respective cathode and anode products. Ammonia remained in solution. He determined some of the electrochemical constants of this compound from which he derived its heat of combination. Peratoner and Oddo,[7] in the belief that the nitride ion would discharge as a polymeride, which would prove to be identical with argon, electrolyzed solutions of hydronitric acid and of sodium trinitride.

Szarvasy[8] made a study of the electrochemistry of various hydrides of nitrogen. He electrolyzed solutions of hydronitric acid and sodium trinitride under various conditions of concentration and of current density, and measured the electrode products. He found but a slight variation from the ration of 1 : 3 between the hydrogen evolved at the cathode and the nitrogen at the anode. In some solutions traces of ammonia were obtained after electrolysis.

Browne and Lundell[9] electrolyzed a solution of potassium trinitride in liquid hydronitric acid at —80°. This daring investigation showed

[1] THIS JOURNAL, 26, 577 (1904).

[2] Dennis and Browne, *Loc. cit.*, see page 607; Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876; Curtius, *Ber.*, 23, 3023, also *vide infra*.

[3] Curtius and Rodenhausen, *J. prakt. Chem.*, [2] 43, 207 (1891).

[4] *J. Chem. Soc.*, 77, 705 (1900).

[5] *Ber.*, 32, 3066 (1899).

[6] *J. Phys. Chem.*, 10, 593 (1892).

[7] *Gazz. chim. ital.*, 25, II, 13 (1895); *Chem. Centr.*, 1895, II, 864.

[8] *J. Chem. Soc.*, 77, 503 (1900).

[9] THIS JOURNAL, 31, 435 (1909).

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that while liquid hydronitric acid is a non-conductor itself, like water, liquid ammonia, liquid hydrochloric acid and anhydrous hydrazine, it is an ionizing solvent. The electrolysis of potassium trinitride in the liquid hydronitric acid yielded hydrogen and nitrogen as the respective cathode and anode products, and in the approximate ratio of 1 : 3, corresponding to the ratio of hydrogen and nitrogen in hydronitric acid. The behavior of potassium trinitride in this solution is strictly analogous to that of potassium hydroxide in water solution. In some cases the ratio of 1 : 3 was not obtained, a lower ratio being observed. Appreciable amounts of ammonia were obtained, indicating a reduction at the cathode. And the accumulation in the electrolytic cell of some unstable compound, producing violent explosions, led to the supposition of the possible formation there of the polymer of nitrogen.

Experimental.

In this description of the electrochemical corrosion of metals in sodium trinitride solution, the experiments will be taken up in the order of the electrochemical nature of the metals studied, although this is not their chronological order.

General Procedure.—In the paragraphs immediately following, such statements will be made as apply in general to all the experiments alike. Where the conditions of electrolysis cannot be covered by such a general statement, they will be described under the individual experiment.

Two series of corrosions were made in the case of each metal, in unstirred and in stirred solution. All other conditions, with a few exceptions, were kept approximately constant. The electrolytic bath was a 2 per cent. solution of NaN_3. The salt was obtained from Raschig and was used without recrystallization. The temperature of the electrolytic bath was room temperature, except where it became warm through the action going on within it.

In those experiments where corrosions were studied in unstirred solution, beakers of 350 cc. capacity were employed. Across their tops rested the electrode holder, consisting merely of a block of wood of a convenient size, containing two parallel slits, 3.2 cm. apart. Into the slits were inserted the electrodes. As such supports were employed in every case, the electrodes were always the same distance apart. This factor, therefore, was a constant one.

As the electrodes were not always of uniform size, no general statement can be made covering their dimensions. Where the broad sheet electrodes were in use, their proximity (3.2 cm.) to each other and to the cell walls made it probable that not more than one-third of their outer surfaces was electrochemically active. On the other hand, where the anodes had the form of strips of metal, or of cylindrical sticks, it is very probable that the electrolytic action took place with fair uniformity over their surfaces.

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All other factors which are known to influence current density[1] will be described in the account of the individual experiments.

Where the corrosions were performed in stirred solutions, the latter were contained in beakers of 250 cc. capacity.

In these experiments the agitation of the electrolytic bath was effected in most instances by rotating the anode. Thus, corrosions were studied under conditions of stationary and rotated anodes.

A rotating device was employed which admitted of the electrolysis of five cells in series, each with a rotating anode (or cathode). The electrode to be rotated was fastened by means of a clutch to a pulley, the axis of which was vertical. The five pulleys were actuated by means of belts working over a second set of pulleys mounted on a common axis. The latter was placed horizontally and was rotated by an electric motor.

Electrical connection was made with the metal of the first pulleys and, through it, with the electrode attached thereto; a wire to which could be joined the opposed electrode connected with the metal of the next pulley, and so on. There was additional wiring so arranged that, by means of two-way switches, the electric current could be shunted around any cell or cells, without interrupting the experiment.

As all the parallel pulleys of the machine were of the same size and were operated by belts from a common shaft, the speed of rotation of the anodes, or of the agitation of the electrolytic bath in cases where the anode was not rotated, but the solution was stirred by the rotation within it of some other body, was the same in all five cells. For any one series, then, that factor also was a constant. While the speed of rotation was the same in all five cells at any one moment, it varied from time to time, due to the fluctuations of the current operating the motor. The speed averaged about four revolutions a second, a rate which was sufficient to keep the entire solution within the cell actively whirling.

For cathodes in the stirred solutions, a thin platinum wire was always used. This was immersed to such a depth that the length of its active area equaled that of the anode. As the cathode paralleled the anode, a uniform current density on the latter was assured.

The anodes were carefully cleaned in proper reagents and were dried and weighed. After they had been subjected to the corrosion they were again cleaned as thoroughly as was possible with running water and soft cloths, and were again dried and weighed. In some instances it was not possible by the means employed to free them absolutely from the precipitate formed on their surfaces. To facilitate drying, the electrodes were washed finally in absolute alcohol. Except where the presence of explosive compounds was suspected, the alcohol was burned off; otherwise, it was allowed to evaporate spontaneously.

[1] Turrentine, *J. Physic. Chem.*, 14, 152 (1900).

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Efficiency[1] was calculated on the basis of values obtained from a copper coulometer. The latter was filled with a solution of copper sulfate, acidulated with nitric acid and containing alcohol.[2] The electrodes were stationary copper plates which presented so large an active surface (46 cm^2.) to the electrolytic action that a satisfactory cathode deposit was invariably obtained. The usual method of washing coulometer electrodes was followed, after which they were allowed to come to constant weight in desiccators.

Calculations were based on cathode values.

Magnesium. Unstirred Solutions.—Magnesium anodes were prepared from cylindrical sticks of metal, by splitting. This yielded anodes hemicylindrical in shape and 1 cm. in width on their flat surface.

The anodes were immersed in the electrolytic bath to a depth of 7.5 cm., exposing a surface of 19 cm^2. The cathodes were platinum wires. Two cells were run in series.

During the electrolysis, which was prolonged 1 hr., the solution became filled with a white flocculent precipitate of magnesium hydroxide, or of basic magnesium trinitride.[3] The anodes were loosely coated with the white precipitate. They became roughened and pitted so that it was difficult to remove the last of this precipitate. There was a vigorous evolution of gas from the anodes, which did not cease abruptly with the interruption of the current, but continued at a decreasing rate for several minutes.

The anode losses and efficiencies as determined in four experiments are expressed by these figures: (Expt. 1) 0.2488 g.; efficiency 186.6 per cent. (Expt. 2) 0.0086 g.; efficiency 171.4 per cent.; theory for Expts. 1 and 2 on basis Cu: Mg 0.1333 g. (Expt. 3) 0.2374 g.; efficiency 176.3 per cent. (Expt. 4) 0.2394 g.; efficiency 177.7 per cent.; theory 0.1347 g. (Expt. 5) 0.1957 g.; efficiency 160.4 per cent. (Expt. 6) 0.1798 g.; efficiency 160 per cent.; theory 0.1220 g. (Expt. 7) 0.1917 g.; efficiency 170 per cent. (Expt. 8) 0.1872 g.; efficiency 166.6 per cent.; theory 0.1123 g.

Experiments 1–4, inclusive, were performed in cells of one compartment, as described. Experiments 5–8, inclusive, were carried out under the conditions subsequently to be described. As the conditions controlling current efficiency were approximately the same as those which obtained in experiments 1–4, the values from all eight experiments are reported together.

These figures show that the anode efficiencies approach 200 per cent. Superficially, an evolution of gas at the anode would merely mean imperfect corrosion efficiency, a discharge of some nitride ions instead of the formation of magnesium ions. In view of the fact that an efficiency approaching 200 per cent. was being obtained, this supposition of an imperfect corrosion scarcely looked plausible.

[1] That is, the amount of corrosion compared with that required by Faraday's law.

[2] Oettel, *Z. Elektrochem.*, 1, 57 (1894).

[3] Curtius and Rissom, *J. prakt. Chem.*, 58, 362.

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It has been shown[1] that when magnesium is made anode in sodium sulfate solution, hydrogen is evolved from the anode. In agreement with this, it was supposed that the gas evolved from the magnesium anode in sodium trinitride solution was likewise hydrogen. An experiment was planned, therefore, with a view to the determination of the nature of the anode gases.

The magnesium anodes used in the preceding experiment were thrust through the side arm of coulometer tubes. These were glass tubes, the main length of which, about 50 cc. in capacity, was calibrated. This bore at one end a stopcock, surmounted by a capillary, and at the other end an enlargement, 3.5 cm. internal diameter. The enlarged portion bore the side-arm and was open at the bottom. This constituted the anode compartment. Over the side-arm was slipped a section of rubber tubing which fitted around the protruding end of the magnesium anode and made an air-tight joint. The open end of the tube was then immersed in a crystallizing dish containing a solution of the electrolyte and was surrounded by a parchment diaphragm, extending entirely to the bottom of the cell. This effectually prevented the cathode gases from wandering into the anode compartment. The solution was then drawn up into the coulometer tube until it had entirely displaced the air therein. The cathode was a thin platinum wire.

The electrolysis was prolonged for 1 hr. with a current of 0.3 amp. The current density was variable and was slightly higher than in the preceding experiments.

At the end of the hour the collected gases were drawn off into Hempel burets and were measured. The electrodes were removed and cleaned and their loss in weight was noted. The collected gases were then subjected to analysis for oxygen and hydrogen. The former was measured by absorption over alkaline pyrogallol and the latter, by combustion in the presence of an excess of oxygen in a Hempel-Dennis gas pipet. The loss in volume was taken as representing the volume of hydrogen, plus its equivalent volume of oxygen. Two-thirds of the loss in volume then was taken as hydrogen. Nitrogen was determined by difference.

Four such experiments were performed under practically the same conditions of electrolysis. The results obtained are given in Table I:

TABLE I.

Expt. No.	T. V. Cc.	O_2. Cc.	O_2. Per cent.	H_2. Cc.	H_2. Per cent.	N_2. Cc.	N_2. Per cent.
5	18.2	0.4	2.1	5.4	29.6	12.4	68.3
6	17.0	0.5	2.9	4.6	27.0	11.9	70.1
7	16.8	0.6	3.5	4.6	27.3	11.6	69.2
8	17.7	0.6	3.2	5.4	30.5	11.7	66.3

[1] Turrentine, *J. Physic. Chem.*, 12, 448 (1908); *Trans. Am. Electrochem. Soc.*, 13, 289 (1908).

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In the first series (Expts. 5 and 6) the anode was removed first in Expt. 6, and in the second series (Expts. 7 and 8) in Expt. 7. It has been mentioned that the evolution of gas from the anode continued after the electrolysis had ceased. So, in those experiments (Expts. 5 and 8), where the anodes were left in the solution for a longer time, there was obtained a slightly greater volume of gas. In these instances also there was a larger percentage of hydrogen present. In order to determin the nature of the gas evolved in the manner just mentioned, portions of it were collected and were analyzed.

The evolution after the first few minutes became very slow, so that at the end of 19 hours only 3 cc. had accumulated. On analyzing this volume of gas there was no absorption in alkaline pyrogallol; on combustion, the loss in volume was 4.5 cc., corresponding to 3.0 cc. H_2, the original volume. Attention is called to the fact that the volume of hydrogen evolved by the anode standing for 19 hours in the solution is less than that volume evolved in 1 hour during the electrolysis.

Discussion of Results.—In the light of Faraday's law, the foregoing results from the corrosion of magnesium anodes in sodium trinitride solution show that the electrochemical equivalent of magnesium is twice as great as what we should expect from the usual chemical behavior of that element. The valence manifested here is one instead of two. In no other way are we able to explain satisfactorily the high corrosion efficiency observed.

While magnesium in all of its known salts exhibits bivalence, there are reactions recorded where the metal appears in a hypothetical, unstable, univalent condition. Beetz,[1] on the basis of a suboxide of magnesium, explains certain phenomena observed when he electrolyzed an aqueous solution of magnesium sulfate with magnesium anode. A black substance formed on the anode which gradually reacted with the water to form hydrogen and a precipitate of magnesium hydroxide. Beetz made a series of quantitative measurements of the hydrogen evolved and of the magnesium dissolved from the positive pole and found in every case that the two were equivalent.

Christomanos,[2] on cooling suddenly a flame from burning magnesium, obtained a gray powder, which from its analysis appeared to have the formula Mg_8O_5. Baborovsky[3] regarded the compound obtained by Christomanos as identical with that obtained by Beetz. Luther and Schilow[4] hypothesized a univalent condition of magnesium to explain

[1] *Phil. Mag.*, 32, 269 (1866); *Pogg. Ann.*, 127, 45; Cf. also Elsasser, *Ber.*, 9, 1818 (1876); 11, 587 (1878).

[2] *Ber.*, 36, 2076 (1903).

[3] *Ibid.*, 36, 2719 (1903).

[4] *Z. physik. Chem.*, 46, 803 (1903).

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the reaction which takes place between magnesium, iodine and methyl alcohol whereby hydrogen is evolved.[1] Their supposition of an intermediate reaction in which is formed a *magnesious* iodide is represented by the equation:

$$Mg + \tfrac{1}{2} I_2 = MgI$$
$$MgI + CH_3OH = MgIOCH_3 + \tfrac{1}{2} H_2.$$

In a previous research[2] involving the action of magnesium when made anode in sodium sulfate solution, it was observed that there ensued a vigorous evolution of hydrogen at the anode, continuing for several minutes after the electrolysis had ceased, and that in the anode region a copious precipitate of magnesium hydroxide formed. These phenomena were explained by the supposition that the magnesium went into solution as unstable magnesious sulfate and there reacted with the solvent, water, to form magnesic compounds and hydrogen. This reaction may be represented by the equation:

$$Mg_2SO_4 + 2H_2O = MgSO_4 + Mg(OH)_2 + H_2.$$

This hypothesis accounted for all the observations in a perfectly satisfactory manner.

To explain the excessive current efficiency at the anode when magnesium is made anode in sodium trinitride solution we must suppose, likewise, the occurrence of univalent magnesium. The magnesious trinitride, then, formed at the anode should react with the solvent and evolve hydrogen, in a manner analogous to the reaction of magnesious sulfate. As we have seen from the analysis of the anode gases, only a small amount of hydrogen is evolved, not enough to correspond to the amount of magnesium dissolved in the univalent form. The hydrogen, or its equivalent in reducing power, must be consumed in some reduction.

The only reducible substance present, besides water, is the nitride ion. Szarvasy[3] obtained ammonia as a product of the electrochemical reduction of the nitride ion, or of the hydronitric acid molecule. Curtius and Rissom[4] observed the formation of ammonia when metallic tin and zinc dissolved in hydronitric acid, and Curtius and Darapsky[5] noted a similar reaction when antimony and arsenic dissolved in that acid. Cook[6] reduced hydronitric acid chemically to ammonia and hydrazine by means of such reducing agents as sodium amalgam, zinc and hydrochlóric (or sulfuric) acid, sodium sulfide and ferrous hydroxide. Ammonia was

[1] "Data on the Chemical Role of Catalytic Agents," *J. Russ. Physic. Chem. Soc.*, 35, 399; *Chem. Centr.*, 711, 277 (1903).
[2] Turrentine, *Loc. cit.*
[3] *J. Chem. Soc.*, 77, 603 (1900).
[4] *J. pr. Chem.*, [2] 58, 292.
[5] *Ibid.*, [2] 61, 408 (1900).
[6] *Proc. Chem. Soc.*, 19, 213 (1903).

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the chief product. Hydrazine was found present only where it was protected from further reduction by forming some insoluble compounds, which removed it from the sphere of reaction. The reaction proposed by Cook may be represented by the equation:

$$HN_3 + 3H_2 = NH_3 + N_2H_4.$$

This investigator showed likewise that hydrazine could be reduced to ammonia, thus in a way substantiating his theory. The reduction of hydrazine to ammonia has been observed by other investigators.[1]

Dennis and Doan[2] reduced thallium trinitride to ammonia by heating the salt in a stream of hydrogen; and Dennis and Isham[3] obtained ammonium chloride and nitrogen from the interaction of gaseous hydrochloric and hydronitric acids. Curtius and Rissom[4] obtained the same products when the two acids were allowed to react in aqueous solution.

If the magnesious compound reacted as a reducing agent toward the nitride ion we should have the formation of ammonia, or of ammonia and hydrazine. Such a reaction could be represented thus:

(1) $$12\,MgN_3 + 14H_2O = 5MgN_6 + 7Mg(OH)_2 + 2NH_3 + 2N_2H_4$$

This equation is based on that proposed by Cook.

Or, one of the nitrogens of the magnesious trinitride may be reduced to ammonia and the other two liberated as molecular nitrogen. Equation (2) expresses such a reaction:

(2) $$4MgN_3 + 6H_2O = MgN_6 + 3Mg(OH)_2 + 2NH_3 + 2N_2.$$

This equation is of especial interest because by means of it we are able to account for the large evolution of nitrogen from the anode. It has been noted[5] that one of the nitrogens of hydronitric acid acts differently from the other two.

The anode evolution of nitrogen is explicable on the assumption that some N_3^- ions are discharged. This would mean a low corrosion efficiency, and would be the logical explanation, if an efficiency of less than 100 per cent. had been obtained.

If the corrosion efficiency were based on univalent magnesium the efficiency would be less than 100 per cent. In Expt. 5 the theoretical anode loss at the anode would be $2 \times 0.1220 = 0.244$ g. The observed value being 0.1957 g., there is a deficiency of 0.0483 g. Mg. Under the condition of temperature and atmospheric pressure obtaining at the time of the experiment, this weight of magnesium would be equivalent

[1] In the summer of 1907, in attempts made by the writer to prepare sodium hydrazide by the interaction of metallic sodium and imperfectly dehydrated hydrazine, the formation of ammonia resulted.

[2] THIS JOURNAL, 18, 970.

[3] *Ibid.*, 29, 18 (1907).

[4] *Loc. cit.*

[5] Dennis and Isham, *Loc. cit.*

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to 80 cc. N_2 (Mg : N_3); observed, 14.3 cc. N_2. This represents the maximum amount of nitrogen that could be evolved in this manner.

It is conceivable that the reduction might result in ammonia quantitatively, either directly, or through hydrazine as an intermediate product, as indicated in equation (3):

(3) $16MgN_3 + 18H_2O = 9Mg(OH)_2 + 7MgN_6 + 6NH_3$.

Or, again, reactions as indicated in equations (1) and (2) might take place simultaneously, producing all three substances, ammonia, hydrazine and nitrogen, as reduction products. This reaction may be represented as follows:

(4) $8MgN_3 + 10H_2O = 3MgN_6 + 5Mg(OH)_2 + 2NH_3 + N_2H_4 + N_2$.

In agreement with these hypotheses, the solution in which the corrosions had been performed should have contained ammonia or hydrazine, or both. Accordingly, portions of these solutions were subjected to a quantitative analysis for ammonia by distillation from an alkaline solution. Two such analyses gave identical results. The amount of ammonia present in the total volume of solution (700 cc.) was found to be 0.118 g.

The residue left in the distillation flask was tested for hydrazine with Fehling's solution. Reductions were obtained repeatedly, indicating the presence of the N_2H_4 radical.[1] The distillate, after it had been titrated, was tested likewise with Fehling's solution. No reduction of the test solution was obtained.

These results, while merely qualitative when applied to the question under study, give strong support to our theory accounting for the anomalous behavior of magnesium anodes in sodium trinitride solution. They indicate that the reduction which takes place here, leading to the formation of ammonia, hydrazine and nitrogen, is of the order represented by equation (4). They are also in agreement with the chemical reduction of hydronitric acid as accomplished by Curtius and by Cook.[2]

[1] The reaction with Fehling's solution, of course, is not characteristic of hydrazine alone. In this test it is necessary to suppose the absence of other reducing agents. However, considering the conditions under which the experiments were performed and in the light of the work of other investigators, we believe that we are justified in stating that hydrazine was here present.

[2] One other explanation suggests itself. In examining the action of ammonium persulfate on metals (Turrentine, *J. Physic. Chem.*, 11, 623 (1907)), the author observed that iron dissolved to ferrous sulfate and evolved hydrogen. The ferrous sulfate was oxidized by the persulfate present to ferric sulfate, which hydrolyzed and produced a precipitate of ferric hydroxide. Although, in the beginning, the solution was stoichiometrically neutral, after ferric hydroxide had been formed it reacted acid to litmus paper. It appeared, then, that the evolution of hydrogen from the iron in ammonium persulfate solution might be due to the reaction of the free acid on the iron. Likewise, iron immersed in a solution of ferric sulfate also evolved hydrogen. The solution showed acidity when tested with litmus. Alkaline hydroxides added to this solution precipitated ferric hydroxide, but left the solution still acid.

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A similar evolution of hydrogen was noted also when iron was made anode in ammonium sulfate solution, and a current was passed of such strength as to afford a current density at the anode high enough to cause oxygen to be evolved.

While it is difficult to harmonize the theory advanced with this last phenomenon, yet the mass of evidence points to the reaction of the acid, formed as indicated, on the iron.

In sodium trinitride solution, hydrolysis increases the concentration of the hydroxyl ion and produces alkalinity. However, in the case of magnesium, the coating of precipitated magnesium compound on the anode makes the solution actually in contact with the anode quite independent of the main solution. Its state of acidity or neutrality is not influenced by that of the main solution. If, then, the hydrolysis of the magnesium trinitride liberated sufficient hydronitric acid to bring the concentration of the latter to a point where it would dissolve magnesium, we should expect an evolution of hydrogen were the corrosion taking place *chemically*. The hydronitric acid then would be acting as a catalytic agent in the reaction between magnesium and water. The hydrogen evolved would be free to reduce a trinitride present in its vicinity. This case would be different from that of iron, however, in the particular that here at most only one-half of the hydronitric acid is liberated (assuming that magnesium trinitride, like zinc trinitride, hydrolyzes to the basic trinitride), and would constantly decrease next to the electrode. While these reactions could take place were the corrosion chemical, it is hardly conceivable that they would take place with electrolysis, that free hydrogen could be evolved by a weak acid in dilute solution at an anode where new ions are being formed. The hydrogen liberated by the hypothetical magnesious compound reacting with water, to be sure, takes place in the anode region, but not in absolute contact with the anode as must the reaction between the anode and an acid. While the latter reaction may take place chemically or hydrogen may be evolved potentially, the electrochemical tendency at the anode is to produce new cations, and not to liberate them, and to prevent the discharge of hydrogen. This is tacitly acknowledged whenever we use a copper coulometer filled with an acid solution. While we recognize the solubility, chemically, of the electrodes in the acid of the electrolytic bath, we rely on the electrochemical action at the anode (and cathode) to prevent the chemical action. The weak point in this explanation is that it can be applied only in those cases where hydrolysis occurs; aluminium trinitride hydrolyzes completely, zinc trinitride, to the basic trinitride, and magnesium trinitride, perhaps slightly.

In the foregoing discussion no mention has been made of the possibility of explaining change in valence on the basis of linkage,[1] a possibility which should be considered in assigning valencies to elements existing in combination. Such considerations, however, scarcely apply when the effective valence of an element, based on Faraday's law and the electrochemical equivalents, that valence which manifests itself in electrochemical corrosions, is being dealt with.

Aluminium. Unstirred Solution.—Aluminium anodes were prepared from thin sheet aluminium. Two anodes were employed whose dimensions were respectively 5.5 by 5 cm. and 6.0 by 6.0 cm. Their distance from the cathodes and from the walls of the cell was such that about one-third of the area of their back surfaces was regarded in computing current density. The cathodes were aluminium plates similar to the anodes.

[1] Turrentine, *J. Physic. Chem.*, 12, 448 (1908), see p. 454.

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In some of the experiments the electrolysis was continued for two hours, while in others, for one hour. The strength of the current employed varied from 0.10 to 0.21 amp. No general statement therefore can be made which will cover all the conditions of current density.

There was an evolution of gas from the anode from the beginning of the electrolysis. A white gelatinous precipitate, presumably $Al(OH)_3$, accumulated in the solution.

The anodes, while much roughened, remained comparatively clean and free from precipitate.

The anode losses recorded are given in the following table:

TABLE II.

Expt. No.	Time. Hrs.	Current density.	Anode loss. Gram.	Theory. Gram.	Efficiency. Per cent.
13	2	0.004	0.1033	0.0895	115.0
14	2	0.004	0.1031	0.0895	115.0
15	2	0.003	0.0858	0.0720	119.0
16	2	0.003	0.0861	0.0720	119.0
17	2	0.004	0.1128	0.1949	117.0
18	2	0.004	0.1221	0.1949	128.5
19	2	0.004	0.1175	0.1044	117.3
20	2	0.004	0.1173	0.1044	118.7
21	1	0.03	0.0871	0.0632	138.2
22	1	0.03	0.0863	0.0632	137.0
23	1	0.03	0.0912	0.0713	127.9
24	1	0.03	0.0870	0.0713	122.0

Discussion of Results.—The high current efficiency observed made it appear probable that the aluminium was dissolving at the anode at a valence lower than three and was then reducing the water present, becoming again the trivalent aluminium and evolving hydrogen. This supposition was based on the behavior of aluminium as observed when it is made anode in sodium chloride solution; under these conditions hydrogen is evolved from the anode.[1]

To ascertain the character of the gases evolved from the anode of aluminium, experiments were performed with enclosed anode as was done in the case of magnesium and in an electrolytic cell of the same construction as has already been described.

The anodes were cut from aluminium foil and had the shape of a flat spoon. The diameter of the disc-shaped bowl of the spoon was 3.0 cm. and was something less than that of the coulometer tube forming the anode compartment, while the handle part was sufficiently narrow (0.5 cm.) and long to be thrust through the side arm of the tube. A disc-shaped anode was thus obtained which made possible a fairly uniform current density on its lower face when held in the tube horizontally. A rubber stopper closed the outer end of the side arm. The narrow portion of the

[1] Turrentine, *J. Physic. Chem.*, 12, 448 (1908).

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anode projected out of the side arm past the stopper, but it was sufficiently thin and flexible to admit of the stopper's being inserted firmly and in such a manner as to make an air-tight joint. The outer end was joined to the source of the electric current by means of a split connector. Two such cells were joined in series with each other and with a copper coulometer. The anodes were weighed before and after the electrolysis and t eir corrosion noted. The time duration of the experiment was 1 hr. The current strength was 0.21 amp. The entire lower face of the disc-shaped portion of the anode and about 1 cm. of the narrow portion, equaling a total area of about 7.5 cm^2., constituted the active surface of the anode. With a current of the strength mentioned, a current density was obtained of about 0.03 amp. per cm^2. The results obtained are given below in tabular form:

TABLE III.

Expt. No.	Vol. gas. Cc.	O_2. Cc.	O_2. Per cent.	H_2. Cc.	H_2. Per cent.	N_2. Cc.	N_2. Per cent.
21.....	18.0	1.7	9.4	0.5	2.5	15.8	88.1
22.....	18.6	1.7	9.1	0.7	3.7	17.2	87.2
23.....	17.0	1.0	5.8	..	..	..	..
24.....	18.0	0.9	5.0	0.2	1.1	16.9	95.9

These results show that the gas evolved from an aluminium anode in sodium trinitride solution is essentially nitrogen. Small amounts of oxygen were found invariably, the presence of which can scarcely be ascribed to experimental error. Likewise, traces of hydrogen were indicated, though the values obtained for hydrogen approached the limits of accuracy of the analytical method employed.

It is established that as far as the evolved gases are concerned, the action of this metal in sodium trinitride is not similar to that in sodium chloride solution. It is not easy, however, to account for the excessive anode efficiency of aluminium except by supposing the corrosion of aluminium at a valence lower than its normal valence.

The evolution of hydrogen from an aluminium anode in sodium chloride solution has been accounted for by the theory that the metal goes into solution electrochemically as uni-, or bivalent aluminium (more probably as the bivalent aluminium, thus carrying out its analogy with iron), which is unstable, and then reacts with water, evolving hydrogen. Such a reaction could be expressed by the equation:

$$6AlCl_2 + 6H_2O = 4AlCl_3 + 2Al(OH)_3 + 3H_2.$$

The role of aluminium as a "carrier" in chlorination processes likewise calls for the supposition of an unstable aluminous compound. Norden[1] produces evidence from mineralogical and other sources to substantiate the occurrence of such a form of aluminium. The evolution of nitrogen at the anode, instead of hydrogen, is explainable on the assumption that

[1] *Z. Elektrochem.*, 6, 159 (1899–1900).

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the hydrogen, or its equivalent in aluminous ions, is oxidized by the nitride ion.

This reaction would be strictly analogous to those already illustrated by equations under the discussion of the action of magnesium as anode in sodium trinitride solution. However, in the case of aluminium, the solutions in which the electrolyses had been performed were not analyzed for ammonia and hydrazine, so no new corroboration of the theory can be obtained from that source.

In Stirred Solution.—In the determination of the corrosion of aluminium in stirred solution four measurements were made. As only sheet aluminium anodes were available, the anode was not rotated as was done in the like experiment with magnesium; instead, the solution was stirred vigorously by means of glass rods, attached to the rotating axes of the rotating device already described. The size of the cells made it necessary to place the anodes against the walls of the cells. So, only one face of the anodes was active. The electrolysis was continued for 1 hr. with a current of 0.20 amp. This gave an average current density of 0.006 amp. per cm^2. Gas was evolved from the anode, but no precipitate was formed as in previous experiments.

On weighing the anodes only a slight and varying change of weight was observed; so slight was the change in weight that it was concluded that under the conditions observed in these experiments aluminium becomes passive in sodium trinitride solution.

An examination of the solution in which the corrosion of aluminium anodes had been conducted showed the presence of a soluble aluminium compound. Portions of this solution were evaporated to the point where crystallization appeared. The resulting crystals proved to be only sodium trinitride. The mother liquor was found to contain aluminium in a form from which it could be precipitated by acid as $Al(OH)_3$. Without further experimentation it was concluded that this compound was an aluminate of sodium, formed by the action of the free sodium hydroxide produced during the electrolysis on the aluminium hydroxide present. Curtius[1] observed that the Al^{+++} ion was precipitated as hydroxide by sodium trinitride. The only compound of aluminium that could be present, then, would be one of the type of an aluminate.

In the succeeding experiments, with the exception of those dealing with silver, the formation of a metallic deposit on the cathode may be attributed to the deposition of metallic ions from a compound of the type of an aluminate. This would probably form where the metallic hydroxides are soluble in sodium hydroxide. The latter was always present, through hydrolysis and electrolysis.

Zinc. Unstirred Solution.—The anodes employed were rectangular zinc

[1] *Loc. cit.*

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plates 5 × 10 cm. in dimension. In each case they were immersed to a depth of 7 cm., affording an area exposed to electrolytic action of about 45 cm^2. This includes one-third of the area of their obverse sides. The cathodes were similar plates situated in a parallel position. This should have afforded a uniform current density on the face of the anode. The results obtained are given in the following table:

TABLE IV.

Expt. No.	Time. Hrs.	Current density amps/cm^2.	Anode loss. Gram.	Theory. Gram.	Efficiency. Per cent.	Current. Amps.
29.....	2	0.003	0.5609	0.3212	174.5	0.15
30.....	2	0.003	0.6232	0.3212	191.1	0.15
31.....	2	0.002	0.4100	0.2553	160.5	0.10
32.....	2	0.002	0.4270	0.2553	167.2	0.10
33.....	1	0.004	0.5205	0.3348	150.9	0.20
34.....	1	0.004	0.5264	0.3348	152.6	0.20
35.....	1	0.004	0.6699	0.6348	183.6	0.25
36.....	1	0.004	0.7221	0.6348	197.9	0.25
39.....	55/60	0.04	0.4613	0.2695	171.1	0.28
40.....	55/60	0.04	0.4583	0.2695	170.5	0.28
41.....	40/60	0.04	0.3136	0.1841	170.3	0.28
42.....	40/60	0.04	0.3140	0.1841	170.5	0.28

In Expts. 29–36, inclusive, plate electrodes were employed. In the other four, the anodes were cylindrical sticks of zinc, about 0.5 cm. in diameter. In these four experiments the anodes were exposed to the electrolytic action for about 4 cm. of their length. Their position was such that a uniform current density could not be obtained. The figures for these experiments in the foregoing table, then, represent the mean current density. The theory was calculated on the basis Cu : Zn. There was an evolution of gas from the anode which would tend to show that the corrosion was not quantitative or that some electrode reaction was taking place whereby gas was evolved. The solution became clouded with a white precipitate of zinc hydroxide or of basic zinc trinitride.[1] Most of the precipitate adhered to the anode, forming thereon a thick crust. This was grayish-white in color. A qualitative examination of the anode precipitate revealed the presence of the N_3 radical therein. This would make it appear that this compound is the basic trinitride obtained by Curtius. The anode precipitate was washed repeatedly with distilled water; the wash water continued to give distinct tests for the N_3^- and the Zn^{++} ions, the former in neutral or slightly acid solutions with silver nitrate and the latter with ammonium sulfide. Also, when this precipitate was dissolved in dilute sulfuric acid, effervescence occurred. The evolved gas, by suitable tests, was found to be, in part at least, vapor of hydronitric acid. A precipitate likewise appeared at the cathode of a white gelatinous consistency, which was dislodged by the evolution of

[1] Curtius, *Loc. cit.*

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gas. A loosely adherent, gray-colored precipitate also formed there, which was taken to be metallic zinc.

In order to determin the character of the gases evolved from the anode, electrolyses were conducted with the anode enclosed in a coulometer tube. The apparatus employed was the same as that which was used in the similar experiment with magnesium anodes. A cylindrical, stick anode was thrust through the side-arm of the coulometer tube and was secured by a section of rubber tubing slipped over the end of the side-arm. Two such electrolyses were performed with an oxy-hydrogen gas coulometer in series. The coulometer was of the modified type[1] with adjustable electrodes and leveling bulb, and contained dilute sulfuric acid.

A current whose strength was 0.2–3 amp. was passed for a length of time sufficient to give a convenient volume of gas for analysis. As about 4 cm. of the electrodes were exposed, this current strength gave a minimum density at the anode of 0.03–4 amp. per cm^2. At the completion of the experiment, 42 cc. of gas had been evolved in the coulometer and 10 cc. and 11 cc., respectively, in the anode compartments of the other two cells. As the corrosion efficiency of the zinc in these experiments was not determined, these results are of no value except to show the relative amounts of the gases evolved.

The accumulated gases from the anode compartments were analyzed in the usual way for oxygen and hydrogen. There was no absorption in alkaline pyrogallol nor a loss in volume on combustion. The gas, then, was pure nitrogen.

Four other electrolyses were conducted with a copper coulometer in series. The anode gases were measured and analyzed and the anode corrosion efficiencies were noted. These are presented in Table V.

TABLE V.

Expt. No.	Anode loss.	Theory Zn.	Efficiency. Per cent.	Gas evolved. Cc.
37	0.3448	0.1841	...	44.8
38	0.3168	..	...	40.8
39	0.4613	0.2695	171.1	55.6
40	0.4583	0.2695	170.5	53.6
41	0.3136	0.1841	170.3	40.3
42	0.3140	0.1841	170.5	40.0

Discussion of Results.—These results show that zinc dissolves electrochemically in sodium trinitride solution more nearly as the univalent zinc than as the bivalent form. From analogy with the preceding metals, and from our knowledge of zinc compounds, where the zinc invariably occurs as the bivalent form, if zincous compounds form at the

[1] Turrentine, *J. Physic. Chem.*, 13, 349 (1909); *Trans. Am. Electrochem. Soc.*, 15, 515 (1909).

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anode they probably become at once zincic. This must be accompanied by a reduction. Applying to zinc the hypotheses advanced to account for the anomalous behavior of magnesium and aluminium, we are led to expect the formation of some reduction products of the nitride ion. If the nitrogen evolved at the anode came from the discharge of N_3^- ions, just as when in a sulfate solution, on incomplete corrosion, oxygen is evolved, then we should be able to calculate from the results set forth in Table V how much nitrogen should have been evolved. In Expt. 38 there was an observed anode loss of 0.4613 g. zinc. If there had been a quantitative corrosion as univalent zinc the anode loss would have been 0.5390 g. The deficiency on this basis was 0.0777 g. zinc. The N_3^- ions discharged should give an amount of nitrogen equivalent to this weight of zinc, which would be 0.052 g. N_2; at 27° and 740 mm. pressure (the conditions of temperature and pressure under which the measurements were made) this weight of nitrogen would occupy a volume of 47.2 cc. The observed volume was 55.6 cc.

The calculated value of 47.2 cc. represents the maximum amount of nitrogen that could be evolved through the discharge of the N_3^- ions. Furthermore, it is hardly to be supposed that there is a quantitative corrosion as the unstable univalent zinc. How much zinc dissolves as univalent and how much as bivalent is of course unknown and is indeterminate. As there is obtained experimentally a volume of nitrogen in excess of the maximum calculated, there must be some evolved by a secondary reaction taking place at the anode. Such a reaction has been illustrated in preceding paragraphs. Calculations were made to determin how much ammonia would have been formed from the reduction of hydronitric acid by the amount of univalent zinc produced in the various electrolyses with zinc anodes, computing all the zinc dissolved as univalent zinc. This amount was found to be 0.19 g. The solutions in which these electrolyses had been conducted were mixed and 100 cc. portions were taken for analysis for ammonia. The total volume was 700 cc. On the bases of the results obtained in two analyses, it was found that the total amount of ammonia present was equal to 0.13 g. All tests for hydrazine made on this solution with Fehling's solution gave negative results.

In Stirred Solution.—The anodes used in the experiments about to be described were cylindrical sticks of zinc. They were exposed to the electrolytic action for a depth of 6 cm. Being 0.5 cm. in diameter, they afforded an active area of about 9.5 cm^2. each. The anodes were rotated.

The electrolysis was continued for one hour with a current whose strength was 0.25 amp. This afforded a current density of 0.026 amp. per sq. cm. The anodes became encrusted with a coating of precipitate which was fairly adherent. Five cells were electrolyzed in series with a copper coulometer. On the cathode value of the latter

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the theoretical loss was 0.3381 g. The observed losses and efficiencies were as follows: (Expt. 43) 0.5994 g.; efficiency 177.3 per cent. (Expt. 44) 0.6200 g.; efficiency 183.3 per cent. (Expt. 45) 0.5888 g.; efficiency 174.2 per cent. (Expt. 46) 0.6004 g.; efficiency 177.6 per cent. (Expt. 47) 0.5750 g.; efficiency 170 per cent.

Iron. Unstirred Solution.—Rectangular sheet iron anodes 10 × 5 cm. were used in these corrosions. They were immersed to a depth of 7.5 cm. Cathodes similar to the anodes were placed in a parallel position and 3.5 cm. distant. The electrolyses were continued for a period of 2 hrs. with a current of 0.1–0.15 amp., affording an anode current density of 0.002–0.003 amp. per sq. cm.

In the beginning of the electrolyses the solutions became blood-red in color, due to the formation of ferric trinitride. However, as the experiments were continued, this color was superseded by the greenish color of impure ferrous hydroxide. Gas was evolved from the anode in every case. The cathode was coated with a greenish precipitate of, presumably, ferrous hydroxide. The anodes in two cases were covered with a uniform coating, firmly adhering, jet black in color. This turned dark red on drying in the air. The third anode on its removal from the solution was coated with a glossy, dark red coating.

On replacing an anode in the solution without first removing the coating just described, it was found that the iron had become passive.

The theoretical values were calculated on the basis of both bivalent and trivalent iron. These were found to be: 0.2743 g. as Fe^{++} and 0.1831 g. as Fe^{+++}. The observed values are: (Expt. 48) loss 0.1745 g.; efficiency 63.6 per cent. as Fe^{++}; 95.3 per cent. as Fe^{+++}. (Expt. 49) loss 0.1998 g.; efficiency 72.8 per cent. as Fe^{++}; 109.1 per cent. as Fe^{+++}. The theoretical values calculated are: 0.2743 g. as Fe^{++} and 0.1831 g. as Fe^{+++}. (Expt. 50) loss 0.0045 g.; efficiency 2.0 per cent. as Fe^{++}; 3.1 per cent. as Fe^{+++}; theory 0.2178 g. as Fe^{++}; 0.1449 g. as Fe^{+++}. The low value in Expt. 50 is explained on the supposition that the anode soon became passive. The deep red coating found on it was probably ferric oxide.

Stirred Solution.—Stick electrodes were employed whose cross section was a square, 0.6 cm. on an edge. One end was machined so that it could be inserted into the clutch on the rotating device. They were covered by the solution to a depth of 7 cm., thus exposing an area of 16.8 sq. cm. to the electrolytic action. The anodes were rotated. Five cells were joined in a series with each other and with a copper coulometer. The electrolyzing current, of 0.175 amp. strength, was passed for 1 hr. There was no change in the appearance of the solution nor in that of the anodes. The loss in weight observed in each case was (Expt. 51) 0.0001 g.; (Expt. 52) 0.0001 g.; (Expt. 53) 0.0002 g.; (Expt. 54) 0.0004 g.; (Expt. 55) 0.002 g. These results show that iron, like aluminium, becomes passive when made anode in a stirred solution of sodium trinitride.

Nickel. Unstirred Solution.—Sodium trinitride solution was electrolyzed between electrodes of sheet nickel, the dimensions of which were 5 × 10 cm. The electrodes were 3.5 cm. apart and were parallel and opposite to each other. The dimensions of the portion exposed to the electrolytic action was 5 cm. × 7 cm. Including one-third of the back of the electrodes, the active area would be about 47 sq. cm. A current of 0.1–0.15 amp. strength was passed for 2 hrs. This would afford a current density at the anode of 0.002–0.003 amp. per sq. cm. Gas was evolved from the anode. There was no alteration in the appearance of the anode nor in that of the solution. The cathode, however, became coated with a brilliant black deposit, resembling that which is obtained on a nickel cathode when a solution is electrolyzed which contains both nickel and arsenic. On the back of the cathode where the deposit was thin and of a varying thickness, iridescent effects were produced. The anode losses recorded were as follows: (Expt. 56) 0.0050 g.; efficiency 2.0 per cent. (Expt. 57) 0.0045 g.; theory on basis

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Cu: Ni 0.2928 g. (Expt. 58) 0.0198 g.; efficiency 8 per cent. (Expt. 59) 0.0016 g.; theory 0.2348 g.

These figures show that nickel anodes in sodium trinitride, as in numerous other solutions, become passive. To see if a change in temperature could decrease in any degree the passivity of the nickel anode, a series of corrosions were run in hot NaN_3 solution. The solution was kept at its boiling point during the experiments. The current employed gave a density at the anode of about twice that which obtained in the preceding experiments with nickel. The time was 1 hr. The anode losses were: (Expt. 60) 0.0003 g. and (Expt. 61) 0.0074 g.; theory, 0.4055 g. These figures indicate that the passivity of the nickel is even more marked in hot than in cold solution, and signally fail to uphold the analogy in this particular between the nitride and chloride ions.

In Stirred Solution.—The nickel anodes employed in the five experiments here described were cylindrical in shape and were 0.5 cm. in diameter. They were immersed to a depth of 6 cm., thus exposing to the electrolytic action of the current an area of about 10 sq. cm. Six cells, together with a copper coulometer, were joined in series. The anodes were rotated. The electrolysis was continued for an hour with a current whose strength was 0.225 amp. The current density at the anode was 0.02 amp. per sq. cm. There was no precipitate produced in the solution nor was there an apparent alteration in the anode. The anode losses recorded were: (Expt. 62) 0.0006 g.; (Expt. 63) 0.0006 g.; (Expt. 64) 0.0010 g.; (Expt. 65) 0.0004 g.; (Expt. 66) 0.0006 g.; theory 0.2537 g.

Tin. Unstirred Solution.—The anodes employed in Expts. 67–72, inclusive, were made from block-tin sheets. They were 5 cm. wide and extended into the solution to a depth of 9 cm. The backs of the anodes touched the sides of the beaker, so in computing current density only their faces were considered. The active area, then, was 45 sq. cm. Those used in Expts. 73 and 74 were rectangular strips of block tin 0.5 × 1 cm. in cross section and were immersed to a depth of 8 cm. As the cathode was 3.2 cm. distant from the anode, and the latter was about 2 cm. from the cell walls, it is probable that the current density was about the same on all faces. The active area, then, was about 25 sq. cm. In the first six experiments the current density was approximately 0.0006 amp. per cm^2.; in the last two, it was 0.012 amp. per sq. cm. The cathodes in each case were copper plates of about 35 sq. cm. active area. The corrosions were prolonged for 1 hr. with a current whose strength was 0.3 amp. There was a constant evolution of gas, presumably nitrogen, from the anode. The anodes acquired a black coating, partially removable with a wet cloth, which was iridescent on the black where it was thin and of a variable thickness. A gray deposit, but slightly adherent, resembling metallic tin, formed on the cathode. The results obtained were as follows: (Expt. 67) anode loss 0.0863 g.; efficiency 13 per cent. (Expt. 68) anode loss 0.0954 g.; efficiency 14.3 per cent.; theory on basis Cu: Sn 0.6647 g. (Expt. 69) anode loss 0.0241 g.; efficiency 29 per cent. (Expt. 70) anode loss 0.0536 g.; efficiency 6.5 per cent.; theory 0.8319 g. (Expt. 71) anode loss 0.0471 g.; efficiency 5.7 per cent. (Expt. 72) anode loss 0.0298 g.; efficiency 3.6 per cent.; theory 0.8243 g. (Expt. 73) anode loss 0.0360 g.; efficiency 5.4 per cent.; theory 0.6647 g. (Expt. 74) anode loss 0.0910 g.; efficiency 10.9 per cent.; theory 0.8219 g.

The anode deposit was not analyzed. While it may have been a nitrogen compound of tin, at first it was regarded rather as a film of finely divided tin, produced through the slight disintegration of the anode.

Stirred Solution.—Cylindrical anodes of block tin were employed whose average diameter was about 0.5 cm. Being immersed in the electrolytic bath to a depth of 7 cm., they afforded an active surface of 11 sq. cm. The anodes were rotated. Five

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cells were electrolyzed in series with each other and with a copper coulometer. A current of 0.15–2 amp. was passed for 1 hr. The current density at the anode was 0.013–8 amp. per sq. cm.

In every instance the anodes were covered with a black deposit as was observed in the electrolyses in unstirred solution. The losses at the anode were comparatively slight, in only one instance giving an efficiency as high as 5.7 per cent. (Expt. 77). The losses observed were as follows: (Expt. 75) 0.0078 g.; (Expt. 77) 0.0236 g.; (Expt. 78) 0.0126 g.; theory 0.4095 g. In Expt. 76 there was a gain in weight at the anode of 0.0313 g. and in Expt. 79 of 0.0050 g. The gain in weight instead of a loss observed in two experiments would indicate that the anode deposit was a nitrogen compound of tin instead of a coating of finely divided metal.

Lead. Unstirred Solution.—Two anodes of sheet lead were exposed to the electrolytic action of the electric current for 2 hrs. They were 3 cm. in width and were immersed to a depth of 7 cm. This gave an active surface, including one-third of the obverse side, of about 28 sq. cm. The cathode was a copper plate 3.2 cm. distant and in a parallel position. The strength of the current employed was 0.1–0.15 amp. and gave a current density at the anode of 0.0045 amp. per sq. cm. Gas was evolved at the anode. While there was no precipitate found in the electrolytic bath, there was an accumulation in the bottom of the cell of a solution of a distinct yellow tint and evidently of a greater specific gravity than the rest of the bath.

At the end of the experiments a loosely adherent deposit, of a reddish brown color, had formed on the anodes. This resembled lead peroxide. On examination, however, it was found to dissolve readily in dilute nitric acid, with effervescence, and in sulfuric acid more slowly, also with effervescence. These facts would show that this compound was not an oxide but rather a trinitride, or other nitride, of lead.

The cathode became covered with a thin, but a uniform and adherent deposit of lead (by inspection).

The anode losses observed were slight; they were: (Expt. 80) 0.0142 g. (1.3 per cent. efficiency); theory on basis Cu: Pb 1.068 g. (Expt. 81) 0.0429 g. (5.07 per cent. efficiency); theory 0.8452 g.

Stirred Solution.—The anodes here employed were rectangular pieces of sheet lead 0.2 cm. in thickness; one end was cut down to fit the clutches whereby they were attached to the rotator. They were 0.7 cm. in width and extended into the solution to a depth of 6.5 cm. This afforded an active area of 11.5 sq. cm.

The anodes were rotated. The electrolyzing current had a strength of 0.22 amp. The current density at the anode, then, was about 0.02 amp. per sq. cm. The duration of time was 1 hr.

As in the previous experiments with lead, the anodes were lightly coated with the reddish brown deposit. In every number but one of this series of experiments there was a gain in weight of the anode, instead of a loss. The results observed were: (Expt. 82) anode gain 0.0012 g.; (Expt. 83) anode gain 0.0016 g.; (Expt. 84) anode gain 0.0004 g.; (Expt. 85) 0.0004 g.; (Expt. 86) anode loss 0.0001 g.; theoretical loss on basis Cu: Pb 0.922 g.

These results uphold our supposition that the anode deposit is a nitrogen compound of lead, and tend to show that, with rotating anode, there is a deposition of nitrogen on the anode, probably as the nitride ion in combination with lead, instead of a solution of lead.

Cadmium. Unstirred Solution.—Cadmium anodes were constructed of rectangular strips of metal whose cross section was 1 × 0.5 cm. For a depth of 8 cm. they were covered by the electrolytic bath, thus exposing an active area of 25 sq. cm. The shape of the anodes and their position relative to the cathode and the cell walls make it

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probable that the current density at the anode was fairly uniform throughout the exposed surface. With a current of 0.3 amp. in strength, the anode current density was about 0.012 amp. per sq. cm. For cathode, a copper plate was employed. The electrolysis was continued for 1 hr.

There was a vigorous evolution of gas from the anode. A voluminous, white precipitate formed which, without analysis, was taken to be cadmium hydroxide. Curtius has prepared the normal trinitride of cadmium, soluble in water. A subsequent examination of the solution used in the electrolysis showed the absence of the Cd^{++} ion, from which it must be concluded that the cadmium dissolved from the anode had been precipitated quantitatively by the sodium hydroxide formed at the cathode. The anodes when removed from the cell were quite free from adhering precipitates and revealed a striking crystallin structure, invisible before their corrosion.

The observed losses and anode efficiencies were: (Expt. 87) 0.6467 g.; theory on basis Cu : Cd 0.6611 g.; efficiency 97.8 per cent. (Expt. 88) 0.8008 g.; theory 0.7753 g.; efficiency 105.2 per cent. (Expt. 89) 0.7989 g.; theory 0.7776 g.; efficiency 102.7 per cent.

It is surprizing that, with an efficiency of 100 per cent. at the anode, there should be in addition a vigorous evolution of gas. This was observed also where the corrosion exceeded 100 per cent. While a slight excess over 100 per cent. at the anode could be overlooked, or laid to faulty experimentation, the excessive anode efficiency and the simultaneous evolution of gas make it necessary to apply to this anomaly the same explanation that has been applied to the case of magnesium, aluminium and zinc, where the same phenomena are observed. In accordance with this theory, then, cadmium corrodes as both cadmous and cadmic trinitrides. The former is very probably unstable. In breaking down to the bivalent form it may react with water and evolve hydrogen, or it may act as a reducing agent toward the nitride ion. Morse and Jones,[1] by heating with metallic cadmium the respective halides of cadmium, prepared a substance which had the composition typified by the formula Cd_4Cl_7, probably a mixture of cadmous and cadmic compounds. This exhibited strong reducing properties, reducing Hg^{++} to Hg^{+} and metallic mercury; a reaction with water produced well defined cadmous hydroxide.

This element, occupying a position in the periodic system between mercury, which forms two series of stable salts, and zinc, which forms only one, exhibits the transitional properties of the two. We should expect to find in zinc, and, perhaps, even in magnesium, latent tendencies to exhibit two valencies.

The examination of the anode gases and of the electrolytic bath for reduction products of hydronitric acid was neglected.

Stirred Solution.—The anodes used in these experiments were similar in shape to those employed in the like experiments with tin. Their area immersed in the sodium trinitride solution was 10 cm^2. The anodes were rotated. Five cells, in series with a copper coulometer, were electrolyzed for 1 hr. with a current 0.25 amp. in strength. The current density at the anode was 0.025 amp. per sq. cm.

The solution became filled as before with a voluminous white precipitate. The anodes again were etched so as to bring out in a most striking manner their crystallin structure.

The anode losses and efficiencies were: (Expt. 90) 0.5380 g.; efficiency 102.1 per cent. (Expt. 91) 0.5397 g.; efficiency 102.4 per cent. (Expt. 92) 0.5440 g.; efficiency 103.2 per cent. (Expt. 93) 0.5470 g.; efficiency 103.8 per cent. (Expt. 94) 0.5455 g.; efficiency 103.5 per cent.; theory 0.5269 g.

Copper. Unstirred Solution.—In these experiments rectangular copper plates served

[1] *Am. Chem. J.*, 12, 488 (1890).

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as anodes. The area of the portion submerged in the sodium trinitride solution was 30–35 sq. cm. on a face. The cathodes were similar in shape and size to the anodes and were similarly placed. The electrolysis which was continued for 2 hrs. was effected by a current of 0.1–0.15 amp. The current density computed on the basis of the area of the face, plus one-third of the back, of the anode was about 0.002 amp. per sq. cm.

In the beginning of each experiment the corrosion seemed to be quantitative, as there was no visible evolution of gas from the anode. A voluminous yellow precipitate formed. This would indicate the presence of cuprous compounds, yielding cuprous hydroxide, a fact which can not be compromized with the results obtained by Curtius showing that in the interaction of copper and hydronitric acid only the difficultly soluble, brown-yellow, cupric trinitride is obtained.[1] Early in the electrolysis there invariably appeared on the anode a closely-adhering, black precipitate, and simultaneously an evolution of gas began. From this point the corrosion was no longer quantitative. For this reason the results obtained are of little interest. A subsequent examination of the black precipitate showed that it could be dissolved from the anode readily in dilute nitric acid, with effervescence, and in dilute hydrochloric acid. When dissolved in the latter, the odor of hydronitric acid was observed (CuN_6?). Attempts to remove the precipitate mechanically from the anode, the latter being held under cold running water the while, resulted in an explosion which was accompanied by a deafening report, and was of sufficient violence to inflict injuries on the operator. Curtius regards the cupric trinitride as one of the most unstable of the trinitrides. He remarks that it is explosive when incompletely dehydrated, but does not record that it may explode also when immersed in water. No efforts were made to identify this black compound.

The anode losses and efficiencies observed were: (Expt. 95) 0.1534 g.; efficiency 39.8 per cent. (Expt. 96) 0.1334 g.; efficiency 34.3 per cent.; theory 0.3879 g. (Expt. 97) 0.0854 g.; efficiency 27.7 per cent. (Expt. 98) 0.0052 g.; efficiency 1.6 per cent. (Expt. 99) explosion. (Expt. 100) 0.1585 g.; efficiency 64.4 per cent.; theory 0.2475 g.

The electrolytic bath, on the subsidence of the precipitates, was of a yellow color. On standing it assumed a dark brown color along its surface where it was in contact with the air.

Stirred Solution.—Cylindrical anodes were employed in these experiments. They were immersed to such a depth that an area of about 12 sq. cm. was exposed to the electrolytic action. The anodes were rotated.

Five cells were connected in series and a current of 0.2 amp. was passed (Expt. 101–105 inclusive). The current density at the anode was 0.016 amp. per sq. cm.

A precipitate, of a distinct blue color, formed in every case. This is exactly what one would expect under these conditions, as, even if a cuprous compound were formed, it would be oxidized to the cupric form by the oxygen of the air with which the stirring of the solution intimately mixed it. A black precipitate adhering to the anode again appeared. After the electrolysis had continued for 15 minutes an explosion occurred in one cell, shattering the beaker containing the solution. On continuing the electrolysis again, by closing the appropriate switch and thus throwing out of circuit the demolished cell, after 5 minutes a second explosion occurred. On continuing the electrolysis further an explosion occurred about every 5 minutes until all the cells had been demolished. The jarring caused by the rotating device was sufficient to cause the compound of copper to explode, even though the compound was bathed in water solution.

Silver.—Having in mind the analogy that has been referred to as existing between the nitride and halogen ions, and also the insolubility of the

[1] The reaction between copper and hydronitric acid is now being studied in the Wesleyan laboratory and will be reported in an early communication.

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silver salt of hydronitric acid, it was deemed possible that the N_3^- ion could be deposited electrochemically on a silver anode in a manner similar to that in which Smith and his collaborators[1] have deposited those other ions quantitatively which form insoluble salts with silver.

The analogy between the N_3^- and, for example, the Cl^- ions, is based on the following considerations: (1) The similarity in properties between the silver and the mercurous salts of the N_3^- and the Cl^- ions. (2) Curtius[2] has compared the solubilities of the halogen salts of the metals of the alkali, and of the alkaline earth group with those of the trinitrides of these elements. In the series, Na, K, Rb, Cs, NH_3 and Tl, the comparison places the N_3^- ion between Cl^- and Br^-, and in the series Ba, Ca, Sr and Li, between Cl^- and F^-. (3) The *ionic* weight of the N_3^- ion falls between those of the F^- and Cl^- ions, and more nearly approaches that of the latter. (4) The relative position of nitrogen and the halogens in the periodic table would lead one to conclude that an anion in which nitrogen existed alone would possess properties analogous to those of the halogen ions.[3] Curtius[4] prepared carbonyl trinitride, $CO(N_3)_2$, an analog of carbonyl chloride.

The Precipitation of the Nitride Ion on a Silver Anode.—The anode used in these experiments was a platinum electrode, silver-plated. It was disc-shaped, perforated, and was supported by a stem of platinum wire, attached to the center of the disc. By means of the stem, the anode was fastened to the vertical shaft of a small electric motor. The area of the anode, counting both faces, was about 20 sq. cm. The cathode was a thin platinum wire immersed in the solution to a depth of about 3 cm.

Accurately measured volumes of a standard solution of sodium trinitride (1 cc. = 0.0004 g. NaN_3) were diluted to a convenient volume, (about 150 cc.) with distilled water. The amounts of sodium trinitride taken were sufficient to give a convenient weight of silver trinitride.

With anode rotating, a current of about 0.02 amp. was passed until the precipitate formed on the anode began to darken. The anode was then removed, and was washed, dried and weighed.

In every instance the increase in weight at the anode was slight (0.7–2.0 mg.) below the theoretical increase calculated from the amount of N_3^- ion present. The anode precipitate was not very adherent, but was dislodged to a slight extent and caused a cloudiness in the solution. When the anode was immersed for an instant in dilute (*N*) nitric acid, the precipitate dissolved therefrom with effervescence and the loss in weight

[1] Hildebrand, THIS JOURNAL, 39, 447; E. F. Smith, "Electro-Analysis," 4th ed., p. 297, *et seq.*

[2] Curtius and Rissom, *J. prakt. Chem.*, 58, 306.

[3] Cf. also Dennis and Browne, THIS JOURNAL, 26, 607 (1904); Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876.

[4] *Ber.*, 27, 2684.

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was in some cases as much as 0.023 g. This fact is mentioned to show that while the actual gain in weight at the anode was slight, the amount of silver trinitride formed there was considerable. This could only mean that some silver was removed from the anode during the electrolysis. Another test applied to this precipitate showed it to be a trinitride. An examination of the solution showed that traces of N_3^- ions were still present. As was anticipated, the OH^- ion had supplanted the N_3^- ion on the impoverishment of the latter and, by causing oxygen to be evolved at the anode, had oxidized the silver to the oxide, as shown by the darkening in color of the anode deposit. This complication was avoidable by the use of the Hildebrand cell[1] or by substitution a solution of hydronitric acid for that of the sodium salt. The latter was preferred. Accordingly, then, a very dilute solution of hydronitric acid[2] was electrolyzed in the manner just described.

In these experiments a dark gray precipitate was observed on the needle-shaped cathode. A microchemical examination of this substance showed it to be *metallic silver*. The solution was rendered cloudy by the presence of a precipitate. This latter was filtered out; on examination, it was found to be a mixture of silver trinitride and metallic silver.

In one experiment where the motor stopped and the anode became stationary, the cathode deposit "treed" until it came into contact with the anode. Dilute solutions, it will be remembered, favor the phenomenon of "treeing." The hydronitric acid invariably was found to be decomposed completely by the end of the second half hour of electrolysis. On discovering the probable presence of a soluble compound of silver, as was strongly indicated by the formation of a cathode deposit of silver, attempts to precipitate the N_3^- ions quantitatively on a silver anode were abandoned until a time when this phenomenon could be explained and avoided. Instead, corrosions were determined as with previous metals.

Corrosion of Silver Anodes in Hydronitric Acid Solution.—The silver anodes were strips of silver foil, 1.3 cm. in width. They projected into the solution to a depth of 6.0 cm., affording an active surface of about 8 sq. cm., on a face. The anode was suspended against the sides of the beaker. Only the face, then, was exposed to the action of the current. The cathode was the silver-plated, rotating, platinum electrode used in the previous experiments. This was rotated and the solution was stirred thereby. The electrolytic bath was a very dilute solution of hydronitric acid (1 cc. 0.0003 g. NH_3, approx.).

The current in the beginning of Expts. 106 and 107 was 0.1 amp. in strength, but as the electrolysis continued, and the concentration of the hydronitric acid decreased, the current diminished. The anode density was about 0.016 amp. per sq. cm. In Expts. 108–111, inclusive, the current strength varied between 0.045 and 0.015 amp.

Efficiencies were based on values obtained from a copper coulometer electrolyzed in series with the test cell.

[1] Hildebrand, *Loc. cit.*

[2] The exact strength of this solution electrolyzed is not known as only the amount of the hydronitric acid present was made note of, and not the concentration.

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A slimy white precipitate of silver trinitride formed on the anode and was dislodged by the agitation of the electrolytic bath. This disclosed a dark gray precipitate beneath of a different consistency, which was more firmly adherent to the anode but which could be removed on gently rubbing.

In every instance there was a deposit on the cathode. In preparing the cathode to be weighed, however, most of this precipitate was unavoidably removed. As the cathode gains recorded, for that reason, do not show the weight of the deposit on the cathode, they will be omitted here.

The anode losses and efficiencies observed are given in Table VI.

TABLE VI.

Expt. No.	Time duration. Min.	Anode loss. Gram.	Theory. Gram.	Efficiency. Per cent.
106	..	0.0307	0.0282	108.8
107	..	0.0460	0.0363	127.7
108	67	0.0479	0.0440	108.8
109	30	0.0380	0.0306	124.5
110	30	0.0745	0.0764	95.5
111	30	0.0512	0.0420	121.5

The hypothesis of an occurrence of silver of a valence lower than that normally displayed, offered in explanation of the excessive anode efficiency observed here, has abundant substantiation from the work of others with this element. The occurrence of the sub-halogen compounds of silver has been established by photochemistry. From a solution of silver fluoride, silver subfluoride, or argentous fluoride, is deposited on the anode. Also, in a concentrated solution of silver fluoride, metallic silver forms argentous fluoride. In the presence of an excess of water, the argentous fluoride breaks down again to the argentic, with the precipitation of metallic silver and the evolution of heat.[1] The occurrence of an oxide of silver where the silver possesses a valence lower than one is much mooted. Conspicuous among those who have published results in support of its occurrence are Wöhler,[2] Von Bibra,[3] Cavillier,[4] and Guntz,[5] while its occurrence is attacked by a number of investigators, conspicuous among whom are Bailey and Fowler,[6] Newberry,[7] and Lewis.[8]

The case of silver, however, is markedly different from those studied which lie at the other end of the electrochemical series. While in the case of magnesium, zinc and aluminium, from electrochemical considerations we should expect a strong reduction when the metal undergoes the change from a lower to a higher valence, in that of silver we should look for

[1] Guntz, *Compt. rend.*, 110, 1337 (1890).
[2] *Ann.*, 30, 1 (1839).
[3] *J. prakt. Chem.*, 120, 39 (1875).
[4] *J. pharm.*, 1830.
[5] *Compt. rend.*, 138, 996 (1899).
[6] *J. Chem. Soc.*, 51, 416 (1887).
[7] *Am. Chem. J.*, 8, 196 (1886).
[8] THIS JOURNAL, 28, 139 (1906).

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merely the precipitation of metallic silver, unless, indeed, there were some substance present easily reduced. The equation expressing such a reaction could be written: $Ag_2N_3 = AgN_3 + Ag$.

The presence of the dark gray precipitate observed under the precipitate of silver trinitride, in close proximity to the metal of the anode and markedly distinct from the silver trinitride, suggests the possibility of this being the metallic silver produced by the breaking down of the hypothetical subtrinitride. This finely divided precipitate would be acted on electrochemically and converted into trinitride again, so that we should always have a deposit of silver trinitride covering the deposit of silver.

The presence of metallic silver in the precipitate filtered from the solution was explicable as coming either from the supposed anodic formation thereof, or (more probably) from the pulverulent cathode deposit. The presence of a soluble compound of silver in a solution containing the N_3^- ion can be explained in several ways, but the explanations are so completely without substantiation by experimentation that they are withheld until the phenomenon can be investigated further.

In Sodium Trinitride Solution.—When the two per cent. sodium trinitride solution was substituted for the dilute solution of hydronitric acid, the anode loss was very much less marked. The same apparatus as just described was employed. The electrolyzing current had a strength of 0.15–9 amp. At the end of approximately one-half hour runs, the loss was respectively 0.0013 g. and 0.0003 g.; theory, 0.03 g. These results indicate that the unexpected behavior of silver as anode is a function of very dilute solutions.

Summary.

The results presented in this paper may be summarized as follows:

1. Among the ten metals studied, magnesium, aluminium, zinc and cadmium, in 3 per cent. NaN_3 solution, and silver in very dilute hydronitric acid solution, give anode efficiencies exceeding 100 per cent. of the corrosion predicted by Faraday's law.

2. To account for the excessive anode efficiency the assumption is made that these metals dissolve electrochemically, partially at least, at a valence lower than that usually ascribed to them, forming compounds which are readily oxidized.

3. In support of this hypothesis, reduction products of the N_3^- ion, such as ammonia, hydrazine and nitrogen, are formed in the anode region, indicating the production there of some reducing agent.

4. A new reduction of hydronitric acid is supposed which involves the formation of free nitrogen in addition to ammonia, or ammonia and hydrazine, as the reduction products.

5. The metals, nickel and lead, become passive in unstirred solution, while aluminium, iron, nickel, tin, lead and silver become passive, or practically so, in stirred solution.

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THE PHENOMENON OF OCCLUSION IN PRECIPITATES OF BARIUM SULFATE, AND ITS RELATION TO THE EXACT DETERMINATION OF SULFATE.

By John Johnston and L. H. Adams.

Received March 17, 1911.

In a previous publication from this laboratory[1] it was shown that barium sulfate precipitated from acidified solutions of alkali sulfate and chloride is in general contaminated by a number of impurities, the amount of which may be so great as to cause errors in sulfate determinations of one per cent. or more. Thus, precipitates made from acidified solutions of sodium sulfate and chloride contain, *before ignition*: (*a*) chloride, almost certainly as barium chloride;[2] (*b*) sodium sulfate; (*c*) sodium hydrogen sulfate; the amounts of these depend upon (1) the composition of the original solution, (2) the method of precipitation, (3) the length of the interval between precipitation and filtration. On igniting the precipitate, the barium chloride reacts with the sodium hydrogen sulfate as follows: $BaCl_2 + 4NaHSO_4 = BaSO_4 + Na_2SO_4 + 2HCl$; the hydrochloric acid gas escapes, and along with it is lost some *free sulfuric acid* by decomposition of the sodium hydrogen sulfate, if, as is usually the case, the amount of the latter is more than equivalent to the barium chloride originally present in the precipitate. The precipitates, *after ignition*,[3] therefore contain sodium sulfate (part of which is derived from the sodium hydrogen sulfate), and further may contain in certain cases chloride, most probably as barium chloride. The presence of chloride in the precipitate tends, of course, to make the analytical results too high; the alkali sulfate, on the other hand, tends to make the results of sulfate determinations too low, since we are weighing some sodium sulfate, but calculating as if the precipitate were pure barium sulfate. The precipitates from potassium and ammonium salts are entirely similar, except that no ammonium sulfate is found in the ignited precipitate, because it is lost by volatilization during ignition. The impurities in precipitates made from magnesium salts are similar in character, but smaller in amount.

It appeared very desirable to extend our knowledge of the nature of such precipitates, first, because of its intrinsic importance, and second, because of its general interest; for it is highly probable that entirely analogous phenomena are to be met with in the precipitation of many other substances. Consequently the present investigation was undertaken;

[1] E. T. Allen and John Johnston, This Journal, 32, 588–617.

[2] It seems to be impossible to determin with certainty whether alkali chloride is present or not; the evidence indicates that, if it is present, the amount must be, in general, relatively small. cf. *Loc. cit.*, p. 602, footnote.

[3] It is presumed that no barium sulfate was reduced during ignition—a condition easily fulfilled in practice.

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as a result of which, a fairly complete and satisfactory discussion of the various factors which condition this occlusion is now possible.

We have confined ourselves almost entirely to determinations under standard conditions of the "occlusion," *i. e.*, of the total quantity of sodium sulfate in the ignited precipitate. The "volatility," *i. e.*, the amount of sulfuric acid lost during ignition, which is[1] a measure of the quantity of sodium hydrogen sulfate present in the unignited precipitate, is, as was shown in the previous paper, affected in the same way as is the "occlusion" by all the conditions, with the exception of the acidity of the original solution. This was to be expected, since we are dealing with the occlusion of sodium sulfate on the one hand, and of sodium hydrogen sulfate on the other; the amount of each depends upon the concentration of undissociated Na_2SO_4 and $NaHSO_4$ (making the usual assumption that the amount of occlusion is proportional to the concentration of undissociated molecules[2]); the latter in turn depends upon the concentration of acid in the original solution. Moreover, determinations of "volatility" would have entailed more than double the work.

In order to obtain comparable results on the amount of "occlusion," it is necessary that the work be performed under standard conditions; in the experiments to be described it was our aim to vary only one factor at a time: *e. g.*, the salt content of the original solution was varied, while the acid concentration, the rate of precipitation and the time of standing before filtration, were kept constant. The procedure followed is identical with that previously described,[3] except that in the case of the heavy metals, the amount of metal in the final residue was determined by a suitable method. The results given are in terms of the sulfate of the metal, and represent the amount obtained from one extraction. It is not pretended that the figure after the decimal point is significant; it is given merely as it was actually obtained; some of the figures given represent the mean from duplicate experiments, which did not differ from one another by more than 1 milligram.

In the previous work, it was found that the amount of occlusion is influenced by: (*A*) the concentration of metallic chloride in the original solution; (*B*) the concentration of hydrochloric acid; (*C*) the rate of precipitation; and (*D*) the length of the interval between precipitation and filtration. It may here be said that all the available evidence now indicates that the amount of occlusion is dependent upon (1) the composition of the original solution; (2) the fineness of grain of the precipitate, which in turn is conditioned by the degree of solubility of barium sulfate

[1] With low rates of precipitation at least.

[2] Cf. Richards, *Z. anorg. Chem.*, 23, 383 (1900).

[3] Cf. Allen and Johnston, *Loc. cit.*, p. 590; *J. Ind. Eng. Chem.*, 2, 198; *Z. anorg. Chem.*, 69, 108.

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in the particular medium, the rate of precipitation, and the time and manner of standing between precipitation and filtration. The above factors will now be considered separately.

A. Effect of Increasing the Chloride Concentration.

Series of experiments were made, as above described, with sodium, lithium and potassium salts, with the results presented in Table I.

TABLE I.—EXPERIMENTAL RESULTS ON THE EFFECT OF ADDED CHLORIDE ON THE AMOUNT OF OCCLUSION OF ALKALI SULFATE.

Milligrams of alkali sulfate occluded by 2 grams $BaSO_4$.
Total vol. of soln. 350 cc.; 2 cc. 2 per cent. HCl; time of pptn. 4 mins.; time of standing 18 hours.

Sodium.		Lithium.		Potassium.	
Added chloride. Grams.	Occluded sulfate. Mg.	Added chloride. Grams.	Occluded sulfate. Mg.	Added chloride. Grams.	Occluded sulfate. Mg.
0	8.2	0	7.4	0	11.2
5	17.4	5	12.8	5	13.4
10	19.0	25	23.0	10	16.4
20	24.4	50	28.0	40	25.4
30	31.4	70	29.4	80	35.0
50	38.4	100	47.6		
70	47.6				
100	45.8				

It is evident that an increase in the concentration of chloride in the original solution in each case causes an increase in the amount occluded. With sodium the amount occluded appears to reach a steady value when about 70 grams of sodium chloride are present; with lithium and potassium, it appears to be still increasing at the greatest concentrations studied.

In view of the similar behavior of the alkali metals in this respect, and of the fact that these occlusions have no precise or generally applicable physical significance, it seemed sufficient to investigate the occlusion of the other available metals at a few chloride concentrations only. Consequently the occlusion was determined for each sulfate in solutions (350 cc.) containing initially (*a*) 0 gram, (*b*) 5 grams, and (*c*) 25 grams of the chloride; the results are given in Table II.

The figures to which references to footnotes are attached are not strictly comparable with the others; in these cases, the addition of a larger quantity of acid was necessary in order to prevent hydrolysis. It proved impossible to make really comparable experiments with solutions containing ferric iron, owing to the hydrolysis of its salts in solutions containing little free acid; there is little doubt however that the amount of occlusion of ferric sulfate by precipitates of barium sulfate is of the same order of magnitude as that observed with the other metals. This would cause a greater error in an analysis, however, because the occluded ferric sulfate on heating loses all its sulfur trioxide, and consequently is

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weighed as oxide; it is better therefore, before precipitating, to reduce the iron to the ferrous state; it is still better to remove the iron entirely, if this course is possible.

TABLE II.—EXPERIMENTAL RESULTS ON THE AMOUNT OF OCCLUSION OF THE OTHER SOLUBLE SULFATES.

Milligrams of each sulfate occluded by 2 grams $BaSO_4$.
Conditions as in Table I, except where noted otherwise.

Metal.	Formula of chloride.	Occluded sulfate in ppts. from solutions containing: 0 grams chloride. Mg.	5 grams chloride. Mg.	25 grams chloride. Mg.
Cu	$CuCl_2.2H_2O$	13.2	17.6	21.0
Cd	$CdCl_2.2H_2O$	32.4	41.6	63.8
Zn	$ZnCl_2$	12.8	12.2[1]	14.6[1]
Ni	$NiCl_2.6H_2O$	9.6	15.4	20.6
Mn	$MnCl_2.4H_2O$	19.2	29.6	37.0
Al	$AlCl_3.6H_2O$	11.6	17.0	..
Fe″	$FeCl_2.4H_2O$	11.4[2]	25.0[2]	..
Mg	.....	3.0	..	..

In order to facilitate comparison, Table III was prepared by recalculation and interpolation of the results contained in Tables I and II; the figures given therein represent the number of millimols of each sulfate (or of each metal) occluded in 1 gram of a precipitate made from a solution, the equivalent chloride concentration of which was initially (*a*) 0, (*b*) 0.1 *N* and (*c*) 0.1 molar.

TABLE III.—EFFECT OF CONCENTRATION OF THE METALLIC CHLORIDE ON THE AMOUNT OF OCCLUSION OF METALLIC SULFATE.

Millimols of sulfate occluded by 1 gram $BaSO_4$, when pptd. from solns. about 0.003 *N* in HCl, containing the metallic chlorides at the initial[3] concs. (*a*) 0, (*b*) 0.1 *N*, (*c*) 0.1 molar. Time of pptn. 4 mins.; time of standing 18 hours.

Metal.	Millimols sulfate occluded by 1 g. $BaSO_4$. (*a*)	(*b*)	(*c*)
Mg	0.024	...	...
Li	0.033	0.040	0.040
Na	0.029	0.043	0.043
K	0.033	0.035	0.035
Al	0.017	0.02	0.03
Fe″	0.037	0.06	0.09
Ni	0.031	0.05	0.06
Cu	0.041	0.05	0.06
Zn	0.040	0.05	0.06
Mn	0.064	0.08	0.10
Cd	0.080	0.09	0.10

[1] Amount of acid was 5 cc. 20 per cent. HCl. With no added chloride and 2 cc. 20 per cent. HCl, the occlusion was only 2.6 mg.

[2] Amount of acid was 6 cc. 2 per cent. HCl.

[3] The final chloride concentration is in each case greater by about 0.025 equivalent normal.

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This table shows that occlusion occurs with all the metals investigated, *i. e.*, with all the common metals, the sulfates of which are soluble in water; that the amount of this occlusion, expressed in mols, is of the same order of magnitude for all the metals, and is nearly identical for similar metals. It is to be noted, however, that the above figures only represent values deduced from a series of experiments in which we attempted to fix all the known variables except the initial chloride concentration, and have no meaning except when the various conditions prescribed are fulfilled. This reservation applies, *mutatis mutandis*, to all the data on occlusion presented in this paper.

In the literature there are a few isolated experiments on the amount of occlusion by barium sulfate precipitated from solutions containing salts; the results, in so far as they are comparable, agree with ours. It has long been known that barium sulfate precipitated from solutions of ferric salts occludes iron in some form.[1] In 1892 this phenomenon was investigated quantitatively by E. A. Schneider,[2] who obtained results of the same order of magnitude as ours, and found that the percentage amount of iron occluded under given conditions was independent of the total weight of the precipitate; but since his conditions, in so far as they are stated, differ from ours, it is futil to institute quantitative comparison between the results. Others[3] have since that time repeated and discussed Schneider's data, all of whom doubt his conclusion that this occlusion is a case of solid solution. H. J. M. Creighton[4] investigated the occlusion of aluminium sulfate by barium sulfate, and arrived at results similar to those obtained by Schneider, but again not strictly comparable w th ours on account of dissimilarity of the conditions of precipitation. The only other quantitative work known to us along this line is that of Paul Frion,[5] who studied the occlusion when precipitation was made from solutions containing magnesium nitrate or lanthanum nitrate.

The data presented above suffice to show, we believe, that all of the metals investigated—namely, those with soluble sulfates—are occluded by barium sulfate precipitates; that in each case the amount of this occlusion is of the same magnitude under the same conditions of precipitation, and is similarly affected by similar variation of the conditions.

B. Effect of Increasing the Acid Concentration.

The data of the previous paper,[6] which bear upon this point, have been amplified and extended; the mean results are presented in Table IV

[1] *E. g.*, Jannasch and Richards, *J. prakt. Chem.*, 39, 321 (1889).

[2] *Z. physik. Chem.*, 10, 425 (1892).

[3] Küster and Thiel, *Z. anorg. Chem.*, 19, 97; 22, 424 (1899); Ostwald, *Z. physik. Chem.*, 29, 340 (1889); Korte, *J. Chem. Soc.*, 87, 1503 (1905).

[4] *Z. anorg. Chem.*, 63, 53 (1909).

[5] *J. chim. phys.*, 7, 101 (1909).

[6] *Loc. cit.*, Table VI, p. 596.

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and confirm the conclusion that an increase in the acidity causes a slow decrease in the amount of occlusion. A few isolated experiments bearing on this point made with other metals[1] also confirm this conclusion.

TABLE IV.—EXPERIMENTAL RESULTS ON THE EFFECT OF ACID CONCENTRATION ON THE AMOUNT OF SODIUM SULFATE OCCLUDED.

Milligrams of Na_2SO_4 occluded by 2 grams $BaSO_4$.
Total vol. of soln., 350 cc.; time of pptn., 4 mins.; time of standing, 18 hours; amounts of conc. HCl and of NaCl as undernoted.

Solution contains NaCl. Grams.	Solution contains 40 per cent. HCl in cc. 0.1 Mg.	0.5 Mg.	2.5 Mg.	5 Mg.	10 Mg.	50 Mg.
0	9.0	8.4	7.8	4.6	3.6	2.6
5	17.4	13.6	11.6	.	.	3.8
10	19.0	..	..	.	.	4.6

C. Effect of Rate of Formation of the Precipitate.

It had been observed that the occlusion of sulfate[2] is nearly independent of the rate of addition of the precipitant or at least of such variations in rate as would occur in analytical practice. It seemed desirable to test this more thoroughly; accordingly a series of experiments was performed, in which the two solutions diffused together at such a rate that 2 grams of barium sulfate were formed in the course of several days.

Various schemes to ensure sufficiently slow diffusion were tried; the method found most satisfactory was to put the requisit amounts of sodium sulfate and of barium chloride into separate small beakers or crucibles; to lower these very carefully—to prevent premature mixing—into a large bulk of solution, contained in a larger beaker; and then to keep this system continuously at 100° by enclosing it in a steam bath of suitable construction. The solution contained known amounts of hydrochloric acid and sodium chloride; evaporation of solution and condensation of steam were alike prevented by a thin floating layer of paraffin. Under these conditions there formed in the course of some days beautiful transparent crystals of barium sulfate, many of which were 1–2 mm. long. The crystals, after washing until the washings were free from choride, contained no chloride and less than 0.05 per cent. sodium sulfate. This amount does not exceed the probable error in such a determination; consequently we may conclude that barium sulfate when precipitated *very slowly* at 100° is free from contamination.

A few diffusion experiments were tried at room temperature, which, however, were not so successful. Convection currents set up by temperature fluctuations caused too great a rate of diffusion, and this,

[1] See Table II, footnotes.

[2] This does not hold for chloride, the amount of which occluded is markedly increased if the whole quantity of the reagent is added quickly, *i. e.*, in a few seconds. This increase is due to the fact that $BaSO_4$ precipitated quickly is much finer-grained, and consequently absorbs more material.

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combined with the diminished solubility of barium sulfate under these conditions, resulted in the formation of much smaller crystals, which were contaminated to some extent by both chloride and sulfate.

The main purpose in these diffusion experiments was to make large crystals, some physical property of which—as for instance, the refractive index—might be made to afford information regarding the state in which the impurities are present. This purpose was defeated by the discovery that all of the large crystals of barium sulfate prepared in this way contained no appreciable quantity of impurity.

This observation effectually disposes of the idea that the impurities are present in the form of a solid solution; for, if the concentration of such a solution depends upon the time at all, the variation should be in the direction of an increased concentration, whereas we have found a decrease of concentration with time.

D. Effect of Time of Standing.

The data of the preceding paper,[1] relating to this point, were confirmed and extended by a series of experiments in some of which much longer intervals elapsed between precipitation and filtration. In another series the precipitate and supernatant liquid were kept at 100° during the whole time.

TABLE V.—EFFECT OF TIME OF STANDING ON THE AMOUNT OF OCCLUSION.

Milligrams Na_2SO_4 occluded by 2 grams $BaSO_4$.
Time of standing and temperature during that period as undernoted; other conditions as before.

Orig. soln. contained NaCl. Grams.	Temp.	Length of interval. ¼ hr. Mg.	3 hrs. Mg.	18 hrs. Mg.	2 days. Mg.	4 days. Mg.	48 days. Mg.	150 days. Mg	210 days. Mg.
0.....	About 20°	11.8	..	9.0	..	..	8.4	.	.
5.....	About 20°	22.6	19.0	17.4	14.0	12.2	10.4	8.2	7.6
5.....	About 100°	22.6	14.4	13.4	10.6	10.2	..	.	.
10.....	About 20°	27.6	..	17.8	..	..	..	.	.

The mean results, which are presented in Table V, show that the amount of occlusion diminishes notably during the first two days, and progressively, though very slowly, thereafter; that increased temperature causes a greater diminution in occlusion during the first few hours, but is without especial effect thereafter; and that the amount remaining even after long intervals depends on the original amount, and therefore on the composition of the original solution.

The graph obtained by plotting the amounts of occlusion (m) against $\log t$ (t being the length of the corresponding interval in days) appears to be a straight line, so that the relation is given by the equation $m = a + b \log t$, which is equivalent to the equation $t = ce^{km}$. The form of this relation is identical with that of the relations generally used to express

[1] *Loc. cit.*, p. 596.

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diffusion and absorption phenomena. In any case the results of Table V show conclusively that the amount of occlusion would be entirely negligible if sufficient time were given. This shows again that the figures given by Schneider, and by Creighton, and those contained in the tables of the present paper are not absolute physical constants (although they are definit enough under definit conditions); and constitute a further proof that we are here dealing with absorption phenomena and not with solid solution, *a fortiori* not with compounds of any description. It is certain that the diminution of the amount occluded could be materially hastened by shaking or stirring; this was not tried, mainly for the reason that such a procedure would generally be impracticable in careful analytical work.

In the previous paper a few experiments on the effect of digesting the precipitates were described, from which it was concluded that the amount of occlusion, at the end of three hours on the steam bath, is independent of the composition and concentration of the supernatant liquid.[1] This conclusion would ordinarily be correct in analytical work where the acid concentration of the solution is not great, but it does not hold if the solution exerts a marked solvent effect upon the precipitate, as *e. g.*, if hydrochloric or nitric acid is present in considerable amount. This is shown by the following experiments.

Effect of Digesting the Precipitate with Acid.

Precipitates were made in the usual way from solutions containing Na_2SO_4 + 5 g. NaCl + 0.2 cc. 20 per cent. HCl; after standing 18 hours, the supernatant liquid was decanted off, and 50 cc. 20 per cent. hydrochloric acid were poured over the precipitate. After standing thus for 24 hours, the occlusion was determined. The mean result found was 0.43 per cent., as compared with 0.70 per cent., the amount of occlusion after contact with the supernatant liquid for a similar interval. In other experiments, the barium sulfate was precipitated from neutral solution (containing 5 g. sodium chloride), and immediately after precipitation (*a*) 60 cc. 40 per cent. hydrochloric acid and (*b*) 50 cc. conc. nitric acid were added. The amount of occlusion after 18 hours' contact with these solutions was (*a*) 0.32 per cent., (*b*) 0.44 per cent.; whereas, without the acid, the amount is 0.90 per cent.

There is no doubt that the greatly increased rate of diminution of occlusion in presence of these acids is directly due to the increased rate of recrystallization of the precipitate, which is, in turn, a consequence of the notably greater solubility of barium sulfate in hydrochloric and nitric acids.[2] The amount of occlusion is thus greatly reduced by contact

[1] *Loc. cit.*, p. 597.

[2] Banthisch, *J. prakt. Chem.*, 29, 54 (1884); through Seidell's "Solubilities of Inorganic and Organic Substances."

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with a solution containing 60 cc. 40 per cent. hydrochloric acid added after precipitation; but not so much as if the same amount of acid is present in the solution before precipitation. Under these conditions we found only 0.16 per cent., and observed that the amount was practically independent of the time of standing, as might be expected from the fact that precipitates formed in this way are quite coarse-grained, and to that degree less easily purified.

General Discussion of Results.

In the preceding pages it has been shown that precipitates of barium sulfate carry down some, or all, of the other salts present in the solution; that the amount of the occlusion varies (1) with the concentrations of the salts; (2) with the rate of precipitation, solubility of the barium sulfate in the supernatant liquid and with the age of the precipitate at filtration; in a word, it varies with the fineness of the precipitate, which in turn is controlled by the above three factors. Proof of this statement is afforded in a series of papers[1] by von Veimarn which deal with the size and appearance of the particles of barium sulfate, formed by mixing solutions of barium thiocyanate and manganous sulfate, the concentration of which varied between wide limits. His conclusions have a direct bearing on the problem considered in the present paper, and may therefore be briefly recapitulated.

von Veimarn's general thesis is that amorphous bodies are not precipitated as such from solution; *i. e.*, that the particles of so-called amorphous precipitates are always crystallin; and consequently that the differences between the various modifications of the solid state are in degree and not in kind, in the state of aggregation of the particles and not in differences of structure between the particles themselves. Starting from this point of view, he enunciates the theorem that, if a substance *A* (*e. g.*, $BaSO_4$) is formed by the interaction of two solutions *B* and *C* ($Ba(CNS)_2$ and $MnSO_4$), the form in which it appears depends upon the concentration of the ions Ba'' and $SO_4^=$ in the mixture of *B* and *C*, relative to their concentrations in the solution which is saturated with $BaSO_4$ under the conditions of experiment.

To demonstrate this, he mixed a solution of barium thiocyanate with manganous sulfate of the same concentration (which ranged from about 0.0001 *N* to about 7 *N*) and examined the precipitates at frequent intervals. His observations led him to divide the whole range of concentrations into five regions, each of which, of course, merges into the adjacent regions. The dilutions given are those of each solution before mixing; their reciprocals therefore represent approximately (except in the very strongest solutions) the equivalent concentration of Ba'' and of $SO_4^=$ at the moment of precipitation.

[1] P. P. von Veimarn, *Z. Chem. Ind. Kolloide*, 2, 3, *passim*.

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(1) At dilutions greater than 7000, the precipitate does not separate at all.

(2) At dilutions between 7000 and 600, one obtains in the course of time recognizable crystals by the slow transformation of the form originally precipitated, which is that usually known as amorphous. These "amorphous" grains however, equally with the finest grains obtainable by mechanical means, have the power of inhibiting supersaturation. The general behavior within this region is indicated by the following table.

Dilution approx.	Distinct opalescence appears in:	The bulk of the ppt. settles in:	Remarks.
5000	..	1 month	
3000	6–8 hours	24 hours	Initially an ultramicroscopic suspension; transformed after 6 months into good crystals about 0.001 cm. long.
2000	2–3 hours	10–12 hours	Initially fine-grained spherical aggregates, transformed after 6 months into good crystals of smaller size than the preceding.
1000	3–5 mins.	2–3 hours	
600	a few secs.	½–1 hour	

Further experiments at the dilution 2000 showed that the process of recrystallization requires several months, while the direct crystallization requires but a few hours at room temperature, without shaking. On the other hand supersaturation is removed within a few minutes, the length of this interval depending largely on the slowness of diffusion in the neighborhood of the crystal grains.

(3) At dilutions between 600 and 1 the number of good crystals diminishes, and the formation of skeletons and needles increases with increase in concentration. At 200 the skeletons may be about 0.0005 cm. in length, while the size of the needles varies from perhaps 10 μ down to the smallest points visible in the microscope. At a dilution of 10 the precipitate consists entirely of needles; about 1 the formation of amorphous precipitate begins.

(4) At dilutions between 1 and 0.1 one obtains initially jelly-like amorphous precipitates, which may be differentiated into aggregates microscopically; these quickly become turbid, and change into voluminous fine-grained precipitates.

(5) At the greatest concentrations, jellies are obtained, the particles of which initially cannot be differentiated, even with the ultramicroscope: they remain transparent for several hours, but in about 24 hours are transformed into a plastic mass. This does not change its structure in many months when preserved under water at low temperature; but in boiling water a considerable part of it recrystallizes in three weeks, while in a hot concen-

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trated solution of hydrochloric acid, complete recrystallization takes place in a few days.

From the above observations von Veimarn shows in two ways that the "amorphous" precipitates are composed of crystallin material: first, because with increasing concentration—which is equivalent to decreasing relative amounts of Ba″ and $SO_4^=$ in the solution—there is a progressive diminution in the size of the crystals, but no sudden change to amorphous; and secondly because all precipitates are capable of recrystallization. The process of recrystallization consists in the inhibition by the larger crystals of the supersaturation (with respect to them) of the solutions formed by the greater solubility of the smaller crystals.[1] The slowness of this process is plausible, when account is taken of the degree of supersaturation and of the very small absolute amount of material. Naturally too the finest grained material may require considerable time to grow to recognizable crystals.

von Veimarn's papers have been summarized above rather fully because they show that the fineness of the precipitate depends upon the concentration of Ba″ and $SO_4^=$ relative to that of a saturated solution of barium sulfate in the particular medium;[2] or in other words, the fineness of grain is conditioned by the degree of supersaturation of the barium sulfate in the solution. This is confirmed by other observations: thus, whereas von Veimarn obtained in concentrated solutions particles about 5 $\mu\mu$ in diameter, we were able to obtain crystals 1–2 mm. long in diffusion experiments, in which the degree of supersaturation was kept very small, and crystals up to 4 cm. in length have been found in the Teplitz springs in which barium could not be detected by ordinary analytical methods.[3]

Since the size of the crystal particles depends upon the degree of supersaturation, it follows that the degree of fineness of the particles is increased by a rapid addition of the precipitant; is diminished by precipitating in a medium in which barium sulfate is more soluble; and is further diminished, when the precipitate remains in contact with a medium in which it is soluble, by the process of recrystallization, the rate of which depends upon this solubility. Now these are precisely the conditions which affect the occlusion, when the precipitates are made from identical solutions. We are therefore justified in concluding that this occlusion is a phenomenon of absorption at the surface of the grains of the precipitate; and that its amount depends upon (*a*) the composition of the original solution and

[1] See G. A. Hulett, *Z. physik. Chem.*, 37, 396 (1901).

[2] This is equivalent to the statement that diminution of solubility causes an increase in the number of centers of crystallization. It may be noted that the number of centers increases also with the viscosity of the medium; for increased viscosity decreases the motion of the centers, and therefore increases their number, since the total amount of substance precipitated remains the same.

[3] F. Becke, *Min. petrog. Mitt.*, 5, 82 (1883).

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(*b*) the initial fineness of the precipitate and the amount of recrystallization which has taken place.

This explanation, besides accounting for our own results, also accords with those of Richards and Parker[1] and of Hulett and Duschak,[2] who studied the precipitates obtained by mixing solutions of barium chloride and sulfuric acid; moreover it does not conflict with any reliable experimental evidence with which we are acquainted.

These considerations might be applied to elucidate and correlate the enormous number of mineralogical papers dealing with the composition and crystal habit of natural and artificial barite. This would however lead too far at present. It may suffice to mention perhaps the latest of these, a paper by Hilda Gerhart:[3] crystals of barite were made by the action of various solutions on barium chloride through a layer of gelatinous silicic acid; and it was found that alum and nitric acid exert the greatest influence in modifying the crystal habit. Now, these substances are absorbed to a considerable extent by barium sulfate. This renders it plausible that one factor in the modification of crystal habit is the occlusion by the growing crystal of foreign substances from the supernatant liquid.

The Exact Determination of Sulfate.

By the method given in the previous paper,[4] accurate determinations of sulfate are possible only if three corrections are applied, one of which at least—the correction for "volatility"—is somewhat troublesome to determin. Series of experiments were therefore made in order to find out if it be possible by the application of the principles stated above to devise a general method for the accurate determination of sulfate, in which only slight and easily determined corrections should be necessary. This endeavor to find a generally applicable simple method has not been altogether successful; it was found possible to obtain correct results in some particular instances, but in general these were due to a compensation of errors, all of which were small.

In actual analytical work, the only readily variable effective conditions are the acidity of the original solution and of the supernatant liquid, and to some extent the rate of addition of the precipitant; accordingly we attempted by variation of these conditions, to obtain coarse-grained precipitates, and thereby correct results. The attempts, which were made on solutions of sodium sulfate containing in general sodium chloride, are briefly described below, and the reasons of their failure are indicated. The manipulation and methods used, *e. g.*, in treating the precipitate, are identical with those described in the previous paper; the total volume

[1] *Proc. Am. Acad.*, 31, 67 (1898); *Z. anorg. Chem.*, 8, 413 (1895).
[2] *Z. anorg. Chem.*, 40, 196 (1904).
[3] *Min. petrog. Mitt.*, 29, 185–91 (1910).
[4] Allen and Johnston, *Loc. cit.*

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of the solution was always 350 cc. and the time of precipitation about 4 mins., except where it is expressly stated otherwise.

(*a*) Precipitation in Strongly Acid Solution.

When the original solution is strongly acid, the solubility becomes important, as it amounts to over 30 mg. in the most acid solutions used (50 cc. conc. (40 per cent.) hydrochloric acid in 350 cc. solution). The solubility was taken into account: (*a*) by evaporating the filtrate[1] to dryness, taking up with a little water, filtering, weighing separately, and adding this to the weight of the main portion of the precipitate; (*b*) by evaporating the whole solution (with the precipitate) to dryness[1] immediately after precipitation, taking up with water, filtering, washing and igniting as usual. The results of both methods are identical; they are presented in Table VI, in the column headed "$BaSO_4$ found." In Table VI is also given the amount of occlusion wherever it was determined, together with the correction corresponding to the assumption that all of the sodium sulfate found was originally present as $NaHSO_4$, the reaction $2NaHSO_4 = Na_2SO_4 + H_2SO_4$ taking place on ignition of the precipitate, with a consequent loss of half of the total quantity of SO_3 occluded. For such acid solutions, this assumption must be more nearly correct than the simpler one made previously—namely, that the correction is given by $(BaSO_4 - Na_2SO_4)/Na_2SO_4$; on the newer assumption the correction is exactly twice as great as this.

TABLE VI.—SULFATE DETERMINATIONS IN STRONGLY ACID SOLUTIONS.

Orig. soln. contained					Occlusion.		
NaCl. Grams.	40 per cent HCl Cc.	$BaSO_4$ calc. Grams.	$BaSO_4$ found. Grams	Deficit (uncor.). Grams.	Found. Mg.	Correction.[1] Mg.	Error (cor. for occl.).[2] Per cent.
0	25	1.9955	1.9882	7.3	4.4	*6.0*	*—0.06*
5	25	1.9938	1.9810	12.8	.	.	..
5	50	1.9894	1.9902	—0.8	3.2	*4.4*	*0.26*
5	50	1.9965	1.9967	—0.2	.	*4.4*	*0.23*
5	50	2.0022	2.0014	0.8	.	*4.4*	*0.18*
10	50	1.9905	1.9812	9.3	4.6	*6.4*	*—0.14*
0	50[3]	1.9750	1.9811	—6.1	2.1	*3.0*	*0.45*
5	50[3]	2.0076	2.0152	—7.6	1.4	*2.0*	*0.48*

The numbers in the last column represent the percentage error of the determination, after the above correction has been applied. It is evident that this error is nearly constant for any given original solution and tends to be positive; this is easily accounted for by the fact that the precipitates all contained a trace of chloride, the amount of which was not

[1] This is best done in platinum vessels.

[2] On the assumption that the sulfate occluded is wholly $NaHSO_4$.

[3] In these two experiments, precipitation was rapid—in about 10 secs.; they are therefore not strictly comparable with the others.

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determined quantitatively and has not been allowed for. The influence of the chloride is especially marked in the last two experiments, in which the precipitation was made rapidly—in about 10 secs.; this condition is, conformably with what we had previously found by actual determinations of the chloride, favorable to increased occlusion of chloride. Moreover, the concentration of hydrochloric acid would decrease greatly the ionization of the barium chloride, and hence tend to increase the occlusion of the latter, other things being equal; in somewhat stronger acid solution, precipitation of barium chloride might even occur.[1] It is evident however from Table VI that, by making slow precipitations in presence of much free hydrochloric acid (50 cc. 40 per cent. in 350 cc. original solution) and taking the solubility into account, fair results are obtained, especially with solutions containing 5 grams sodium chloride—a quantity such as is very commonly present in actual work. Correcting for occlusion tends to make the results high, because the precipitates are also contaminated with barium chloride, which is not allowed for in that correction. Incidentally it may be mentioned that the manipulation of the precipitates obtained from acid solutions is much easier and more rapid, by reason of their coarseness of grain.

(*b*) **Precipitation by means of an Acid Solution of Barium Chloride.**

For these experiments we made up a solution containing 23 grams $BaCl_2 2H_2O$ in a liter of 10 per cent. HCl;[2] 90 cc. of this solution are required for the precipitation of 2 grams of barium sulfate. In the precipitation, 100 cc. were run slowly (in about 10 minutes) into the boiling and constantly stirred solution of the sulfate. The remaining manipulation was exactly as in (*a*); but the occlusion was not determined. The results follow.

Orig. solution contained.		$BaSO_4$ calc. Grams.	$BaSO_4$ found. Grams.	Deficit (uncor.). Mg.
NaCl. Grams.	40 per cent. HCl. Cc.			
0	0	1.9923	1.9878	4.5
5	0	2.0183	2.0017	16.6
0	25	1.9894	1.9884	1.0
5	25	2.0039	1.9980	5.9

In this method of precipitation, the concentration of the barium chloride is much smaller (2 per cent. as against 10 per cent.) and consequently the amount of chloride occluded is smaller; furthermore, the bulk of the precipitate is formed in a less strongly acid solution than in (*a*), and therefore the occlusion of sulfate is greater. These two influences together make the deficits larger than in (*a*). Consequently this method is not so

[1] The solubility of barium chloride is enormously diminished by hydrochloric acid; for quantitative data see Engel, *Ann. chim. phys.*, [6] 13, 371 (1888).

[2] This corresponds nearly to saturation.

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good as the former, in which all the acid was present in the original solution; it is besides less convenient.

(*c*) Precipitation in Neutral Solution and Subsequent Digestion of the Precipitate with Concentrated Hydrochloric Acid.

In these experiments the precipitation was made slowly in neutral solution; immediately thereafter, the whole was evaporated to dryness, and then digested, with occasional stirring, for 24 hours at 100° with 50 cc. 40 per cent. HCl. It was then evaporated to dryness, taken up with water, filtered and washed as usual. The ignited precipitates were very hard and flinty, thus indicating considerable contamination; this was confirmed on determining the amount of sulfate occluded. The results, after applying the correction for occlusion of sulfate (on the assumption in this case that it was entirely Na_2SO_4), are considerably too high, and indicate the occlusion of considerable chloride in addition to the sulfate, the presence of which was shown directly.

Orig. soln. contained.		$BaSO_4$.	$BaSO_4$.	Deficit	Occlusion.		Error
NaCl. Grams.	HCl. Cc.	calc. Grams.	found. Grams.	(uncor.). Mg.	Found. Mg.	Correction.[1] Mg.	(cor. for occlusion.)[1] Per cent.
0	0	2.0020	2.0023	—0.3	6.4	4.5	0.24
5	0	2.0076	2.0040	3.6	12.5	8.7	0.26

Here, therefore, although the agreement between the amounts of barium sulfate found and calculated is fairly good, it depends upon a compensation of large errors, conditioned by the fineness of the precipitate. Barium sulfate precipitated from neutral solution is extremely fine-grained; the contamination is not removed with sufficient completeness even by digestion for 24 hours with hot concentrated hydrochloric acid. This method is also burdened with the added difficulty of manipulating the very fine-grained precipitates, which exhibit a marked tendency to adhere to all surfaces with which they come in contact.

General Conclusions on the Exact Determination of Sulfate.

The method given by Allen and Johnston gives correct results but has the disadvantage for general analytical work that one must apply three corrections, two of which are somewhat troublesome to determin. This inconvenience is in part obviated by the fact that the corrections are constant for any particular set of conditions, and so need only be determined once for all. A better plan would probably be to calibrate the method by sulfate determinations on *pure dry* sodium (or potassium) sulfate dissolved in a medium as similar as possible to that in which the sulfate to be analyzed is dissolved. Sodium (or potassium) sulfate is easily obtained in a pure dry state,[2] so that the errors inherent in such a method

[1] On the assumption that the occluded sulfate is wholly Na_2SO_4.

[2] By recrystallizing (if necessary) and heating to 200° in an air bath for an hour; its purity may be easily controlled by an accurate determination of its sulfate content.

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of calibration should be very slight, if the conditions of precipitation were reproduced at all closely.

The foregoing experiments show that none of the methods tried is suitable for accurate work because their apparent correctness depends upon a compensation of errors. In the precipitations in strongly acid solutions, however, these errors are all small and the results are consequently reproducible with considerable accuracy; this method might then well be calibrated in the way suggested above. It possesses the advantage, as compared with the method of the previous paper, that it is easier to manipulate and much more rapid; for one may evaporate to dryness *immediately* after precipitation, and the precipitate, being coarse-grained, does not adhere at all to the vessel, is quickly filtered and easily washed; and with less danger of loss in any of the operations. By making concurrent comparison determinations it should be possible in the course of a few hours to determin sulfate with an accuracy of ± 0.05 per cent. in any solution, the composition of which is known approximately—a condition which very frequently obtains in practice.[1] It would of course be preferable always to have the original solution free from the heavy metals and nitrates, as is usually the case in making sulfate determinations.

In conclusion we may express our belief that there is little chance of discovering any exact method which shall at the same time be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors; for the reason that some of the requisit conditions appear to be mutually incompatible.

Summary.

The occlusion by barium sulfate of other sulfates is a general phenomenon. The amount of this occlusion depends upon (*a*) the composition of the original solution, (*b*) the fineness of the precipitate, which in turn is conditioned by the degree of solubility of barium sulfate in the particular medium, the rate of precipitation, and the time and manner of standing between precipitation and filtration. The phenomenon is therefore in all probability an absorption at the surface of the grains of the precipitate, since it is affected by the factors just mentioned.

On the basis of the knowledge gained in this way, attempts were made to find a direct method for the determination of sulfate which should be generally applicable, exact, and require only small and easily determined corrections. We suggest the following procedure: To the solution (300 cc. for a precipitate to weigh 2 grams) add 50 cc. of concentrated hydrochloric acid, heat to boiling, and precipitate, stirring constantly, with a 10 per cent. solution of barium chloride. This should be added at such a

[1] If the composition of the solution is not known, recourse must be had to the method in which all of the corrections are actually determined.

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rate that about four minutes is required in running in the 22 cc. necessary; the rate is best regulated by attaching a suitable capillary tip to the buret containing the barium chloride solution. Evaporate the whole to dryness on the steam-bath (this may be done immediately after precipitation), take up with hot water, filter through paper, wash until the washings are free from chloride, ignite very carefully (so as to obviate reduction) and heat to constant weight over a Bunsen burner. The necessary correction is determined by a concurrent calibration of the method; that is, by dissolving an equivalent weighed amount of pure dry sodium (or potassium) sulfate in a medium such that the resulting solution is as nearly as may be of the same composition as the solution to be analyzed; the sulfate in this comparison solution is then determined precisely as above. The difference between the calculated amount of barium sulfate and that actually found is the correction to be applied to the weight of the precipitate obtained in the actual analysis.

This procedure, as compared with that advocated by Allen and Johnston, is easier and much more rapid; it is however not so generally applicable, but may be used whenever the composition of the solution containing the sulfate to be determined is known approximately; and, we believe, will yield results, accurate to ± 0.05 per cent. of the total sulfate present, in most cases likely to occur in general analytical work.

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ARTIFICIAL CRYSTALLIZATION OF BARIUM SULFATE.[1]

BY H. C. COOPER AND T. S. FULLER; with Crystallographic Study by A. A. KLEIN.

Received April 8, 1911.

Barium sulfate has a conspicuous place in the literature of the artificial production of crystals, because it has been crystallized by several different methods. The largest crystals, some as long as 2 mm., were obtained by Manross[2] in Wöhler's laboratory, as a result of chemical change in the molten condition, *viz.*, by fusing potassium sulfate with an excess of barium chloride and lixiviating the cooled mass. De Schulten[3] obtained crystals by chemical change in aqueous solution, *viz.*, by very slow precipitation. Senarmont[4] got a similar result by heating barium sulfate with hydrochloric acid in a sealed tube at 250° for 60 hours. This has been considered (by Fock[5]) as a solution method, but it seems more likely that we have here to do with a reversible chemical reaction. Ad-

[1] Presented at the December, 1910 (Minneapolis) meeting of the American Chemical Society, see *Science*, 33, 345.

[2] *Ann.*, 82, 349.

[3] *Bull. soc. franc. min.*, 26, 103; *Chem. Zentr.*, 1903, II, 845.

[4] *Ann. chim. phys.*, [3] 32, 155.

[5] Fock-Pope, "Introd. to Chem. Crystallography," Oxford, 1895, p. 77.

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ditional work on the artificial crystallization of barium sulfate is referred to in Gmelin-Kraut's "Handbuch der Anorganischen Chemie."[1]

We have obtained barium sulfate crystals by crystallization from molten solvents, namely, from barium chloride and from sodium sulfate. This method is probably more nearly physical than any of those already described. Ten grams of barium chloride were fused in a platinum crucible and 8 grams of barium sulfate added. The last three grams were added in gram portions and the eighth gram was found to dissolve very slowly with stirring at 1150°, the maximum temperature of the nickel-alloy resistance furnace. When solution was complete the furnace was enclosed and allowed to cool undisturbed for three hours. After leaching the mass with water for twelve hours, by placing it in a beaker into which water was slowly and continuously run, characteristic barite crystals were obtained, some as long as 5 mm. and as wide as 1 mm. These crystals showed a faint trace of chloride when tested by fusion with sodium sulfate, solution in water and addition of nitric acid and silver nitrate. Probably the barium sulfate takes up a minute amount of barium chloride to form mixed crystals.

Again, 9 g. of barium sulfate were stirred into 10 g. of anhydrous sodium sulfate at 1130°, one-gram portions being added at a time. Eight grams dissolved clear, but the ninth caused some opacity. However, after cooling and leaching, crystals were obtained very similar to those from barium chloride and of the same average size. After several hours' washing with a continuous flow of distilled water the crystals gave a faint flame test for sodium, so that the sodium sulfate, like the barium chloride, probably dissolves slightly in the barium sulfate crystals.

The dimensions of the $BaSO_4$ crystals from Na_2SO_4 averaged about the same as those of the $BaSO_4$ crystals from barium chloride.

Microscopic optical-crystallographic determinations of these crystals, as well as of those out of barium chloride, were made by Mr. A. A. Klein, Assistant in the Mineralogical Laboratory of the University of Michigan. Mr. Klein's report is appended.

The length of the crystals appeared to be limited mainly by the size of the crucible, the longest crystals corresponding to the radius of the crucible. Accordingly, we attempted to produce larger crystals by fusing 428 grams of barium sulfate with 535 grams of sodium sulfate at 1070° in a 500 cc. nickel crucible in an injector gas furnace, but the results were unsatisfactory, probably on account of too rapid cooling. We are confident that in a well-shielded resistance furnace of sufficient size, barite crystals as large as those in nature could be prepared. A nickel crucible is unsatisfactory, however, being disintegrated, apparently by reaction with the melt.

[1] II, 2, p. 41 (1909).

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Le Chatelier[1] has stated that the curve representing the melting points of mixtures of sodium sulfate with increasing proportions of barium sulfate consists of three parts, the first corresponding with the formation of isomorphous crystals containing the two constituents in varying proportions, the second to the formation of a double sulfate and the third to the recrystallization of the added sulfate itself. An experiment in which we dissolved barium sulfate in sodium sulfate to about a 10 per cent. solution yielded crystals which, after washing, were examined spectroscopically and found to be practically free from sodium. This does not harmonize with the Le Chatelier observations and a new thermal analysis of the system $BaSO_4$–Na_2SO_4 appears to be desirable.

Crystallographic Study by A. A. Klein.

The material examined was received from Professor H. C. Cooper and labeled (*a*) barium sulfate, recrystallized from $BaCl_2$, and (*b*) barium sulfate, recrystallized from Na_2SO_4. It consisted of some isolated crystals mounted on two slides in Canada balsam, and of fragments and loose crystals.

Under the microscope the crystals are long, tabular and colorless, with frequent indications of parallel growth. They show parallel extinction, which, with the characteristic outline, establishes the crystallization as orthorhombic. Excellent cleavage was observed parallel to the long direction of the crystals. The indices of refraction were determined by the Schroeder van der Kolk method and were found to be very close to that of monobromonaphthalene ($n = 1.648$), inasmuch as a red tint is observed on the side toward the darkened portion of the field, whereas a blue color is noted on the opposit side. This is an exceedingly close approximation to the values of the indices of refraction given by Groth[2] for the D line of the spectrum, $\alpha = 1.6369$, $\beta = 1.6381$, $\gamma = 1.6491$. In convergent light a distinct positive, biaxial interference figure is frequently observed.

The above observations agree fully with those given by Groth for natural barium sulfate, namely, the mineral barite.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE TRANSITION TEMPERATURES OF SODIUM CHROMATE AS CONVENIENT FIXED POINTS IN THERMOMETRY.

BY THEODORE WILLIAM RICHARDS AND GEORGE LESLIE KELLEY.

Received April 8, 1911.

Introduction.

In previous papers[3] from this laboratory it has been shown that the

[1] *Compt. rend.*, 123, 746 (1896).
[2] Groth's "Chemische Krystallographie," 1908, II, 388–389.
[3] T. W. Richards, *Am. J. Sci.*, [4] 6, 201 (1898); Richards and Churchill, Proc.

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transition temperature of a crystallized salt is in some cases so easily observed and so constantly maintained as to form a convenient fixed point of reference for the scale of temperature. The cases of sodium sulfate (32.383°) and bromide (50.674°) and manganese chloride (58.089°) have been studied in detail and found to be very satisfactory in these respects.

Among other substances suggested for this purpose, sodium chromate is especially inviting because two of its transition temperatures are near 20°, a temperature at which it is frequently desirable to verify thermometers.

The outcome of the work on this salt described in the present paper was entirely satisfactory, and gives promise of great practical usefulness to those who are interested in exact thermometric measurement. Nevertheless, the problem was not so simple as it had at first appeared. The wealth of variety exhibited by the hydrates proved at first to be an embarrassment of riches, and led to some preliminary confusion, which has been happily reduced to order. Moreover, the salt is somewhat less easy to purify than the sulfate, and when it is impure, a given percentage of impurity causes a larger error in the transition temperature than in the case of the sulfate. This is largely because the transition is from the decahydrate to tetra- or hexahydrate, instead of to anhydrous salt, so that the amount of solution formed to dissolve the impurities is less, and therefore the concentration of the impurity in the solution is greater. Another difficulty arises from the fact that chromic acid is a weak acid, and hence its salts are easily capable of absorbing acid impurities. This was shown experimentally by passing pure carbon dioxide into the solution. Large volumes of the gas were absorbed, and the solution became perceptibly orange because of the formation of the dichromate. Boiling expels the gas but slowly, because the hydrolysis increases with rise of temperature. Indeed a boiling solution of the purest salt is so much hydrolyzed as to be red in color and to react strongly with phenolphthalein. Probably the passing of pure air, or boiling at low temperature for a long time in a partial vacuum, would be needed to displace all of the carbon dioxide, and even this might not serve. Of course the solution of the salt absorbs hydrochloric acid and other strong acid vapors yet more easily; and even the dry salt, which is unaffected by carbon dioxide, is attacked by stronger substances.

Theoretically the tendency of the solution to hydrolyze offers no ob-

Am. Acad. of Arts and Sciences, 34, 277 (1899); Richards and Wells, *Ibid.*, 38, 431 (1902); 41, 435 (1906); Richards and Wrede, 43, 343 (1907). These five papers are all to be found in full in the *Z. physik. Chem.*, the references being, respectively, 26, 690 (1898); 28, 313 (1899); 43, 465 (1903); 56, 348 (1906); 61, 313 (1908). The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin.

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jection to the use of the salt as a means of fixing a definit point on the thermometer scale, because the Phase Rule, which determins the definitness of the points, does not consider the state in which the substance exists in any of the phases. The feeble nature of chromic acid is annoying and objectionable only for the practical reason that it makes the preparation and preservation of the pure salt more difficult. When the salt has once been prepared in the pure state, it must be carefully guarded in order to preserve its purity.

These difficulties, however, all disappear when the experimenter is forewarned against them; for easily effected precautions are capable of surmounting them all.

Preparation of Pure Sodium Chromate.

Several methods of further purification of sodium chromate were tried. Crystallization as the decahydrate is of no avail as a means of ridding the crystals of their most usual impurity, the sulfate, because this is isomorphous with the chromate. Indeed as will be shown the sulfate tends into the crystals, leaving the mother liquor somewhat purer than before the crystallization. The tetrahydrate is but little more satisfactory as a means of accomplishing the purification, ten successive crystallizations having failed to yield a pure salt. Moreover, inconvenience arises from the fact that it is stable under the solution only between 26° and 62.8°; and because its solubility has only a comparatively small temperature coefficient, the yields are small.

Attempts to prepare the salt by recrystallizing chromic anhydride were likewise abandoned as unprofitable. The best chromic anhydride obtainable was found to contain much sulfate, which was very slow to leave during the particularly wasteful process of its crystallization. In one case twelve successive crystallizations of a kilogram of chromic anhydride gave only a few grams of product which still contained traces of sulfur. These unsuccessful methods are recounted only to save other experimenters the trouble of attempting the same processes.

The sulfate can be quickly eliminated by relying upon the very different solubilities of silver chromate and sulfate. If a chromate is slowly precipitated by silver nitrate in dilute solution, using not quite enough of the precipitant to remove the chromate wholly from the solution, the precipitate contains very little sulfate. The chromate of silver is then thoroughly washed, and easily converted into sodium chromate by treatment with a solution of pure sodium chloride.

This method is, however, somewhat cumbrous and expensive. Therefore without further delay we may pass at once to another available method, the most satisfactory one of all, which depends upon the fact that sodium dichromate may be easily and quickly freed from sulfate by recrystallization. The dichromate is very soluble, and possesses a moderately

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great change of solubility with the temperature; 100 parts of water dissolve 162 parts of the dry salt at 100° and 109 parts at 15°.[1] Since, however, the salt crystallizes with two molecules of water, the actual loss on crystallization is less than would appear from a superficial inspection of these figures. The weight of the crystals separated from a saturated solution between these two temperatures from 162 grams of anhydrous salt dissolved in 100 grams of water is easily calculated from the equation

$$x + \frac{2H_2O}{Na_2Cr_2O_7}\,x + (162 - x)\,\frac{209}{109} = 262,$$

when $x = 87$ grams. Thus more than half of the salt is easily recovered from each crystallization, and if use is made of a wider range of temperature, permitted by the high saturated boiling point (139° with solubility 210 parts to 100 of water) a still larger yield may be obtained. Since the solubility diminishes but slightly below 15°, further cooling is not profitable. Thus the crystallization of this salt is convenient and efficient; and since sodium dichromate is not isomorphous with the corresponding salts either of potassium or of sulfuric acid (the most probable and insidious impurities) crystallization forms an admirable means of purification. The elimination of the sulfuric acid requires only three or four crystallizations if the crystals are separated centrifugally. A large excess of chromic acid causes unnecessary loss, because of the very great solubility of the trichromate,[1] but a small excess is convenient, because the elimination of the dark brownish tint of the trichromate from the mother liquor is a convenient guide as to the purity of the salt.

The crystallized, pure dichromate was treated with *somewhat less than the calculated amount* of pure sodium carbonate, and with the help of the excess of dichromate the carbon dioxide was easily removed by boiling the solution during an hour. From a neutral solution all the carbon dioxide cannot be expelled. The sodium carbonate for this purpose should be prepared by repeatedly crystallizing the purest soda of commerce in porcelain, or better in platinum dishes, until sulfates and chlorides are certainly absent.

The sodium chromate containing a small amount of sodium dichromate, prepared as described above, was neutralized with the help of phenolphthalein by means of a solution of pure sodium hydroxide, made from sodium by allowing this metal to stand in a platinum dish in a desiccator over a dilute solution of the hydroxide.

Some time was spent in determining the conditions under which phenolphthalein gives satisfactory results in the presence of pure sodium chromate. Schreinemakers[2] states that the chromate is neutral to phenolphthalein and recommends the use of this indicator in analyzing solutions of chro-

[1] Stanley, *Chem. News*, 54, 194 (1886).
[2] *Z. physik. Chem.*, 55, 72 (1906).

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mates for excess of either hydroxyl or chromate ion. In our experiments it appeared that the solubility of the indicator in very concentrated sodium chromate solutions is too small under ordinary conditions to permit of a visible reaction with the low concentration of ionized hydroxyl which must exist there. This is especially true when alcoholic phenolphthalein is dropped into a saturated solution of the chromate. In this case the indicator seems to be precipitated by the salt in such form as to dissolve only very slowly on subsequent dilution. This difficulty was avoided by diluting the indicator with pure water in the first place. On the other hand a dilute solution of the salt is easily shown to be appreciably hydrolyzed, the color of phenolphthalein being distinctly visible superposed on the yellow of the salt. Increasing temperature of course causes increasing hydrolysis; in boiling solutions of the purest very concentrated sodium chromate the hydrolysis is sufficiently great to cause a distinctly reddish tint.

As an outcome of these experiments the neutralization was conducted in concentrated solutions of sodium chromate at room temperature, the indicator in dilute solution being added to the separate test portions. To the main mass of chromate, sodium hydroxide was added until the phenolphthalein just began to show its color in the separate test; and then sodium dichromate until the color just disappeared. This solution may have contained a constant and very slight excess of dichromate, but this substance is easily removed by subsequent crystallization being heteromorphous as regards sodium chromate.

The neutral salt prepared in this way may be further purified by crystallizing either as the decahydrate, hexahydrate, or tetrahydrate. The first named phase, $Na_2CrO_4.10H_2O$, is to be preferred on account of economy of material.

To crystallize the salt with four molecules of water the temperature of the solution must be kept above 26°; but at 26° 100 parts of water dissolve 86 parts of sodium chromate whereas at 0° 100 parts of water dissolve only about 32 parts of sodium chromate in equilibrium with decahydrate; hence arises one reason for the greater economy in crystallizing the decahydrate at the lower temperatures. Moreover, a greater rate of purification from every common impurity except sodium sulfate is possible by this method than through the other hydrates. Six or seven crystallizations as the tetrahydrate give only the same degree of purity as three or four crystallizations as the decahydrate.

The decahydrates of sodium sulfate and chromate are isomorphous, as already stated; hence the sulfate must be previously removed by crystallizing the dichromate in the manner already described.

Crystallization of the pure chromate is best carried out at 5° in platinum vessels; and centrifugal drainage, as usual, greatly increases its efficiency

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as a means of purification. After three or sometimes four crystallizations the sodium chromate was found to give a transition temperature which could not be raised by further crystallization. This is, of course, the criterion to be used in deciding how long to continue the purifying operations. The difficulties attending the purification of this substance are no greater than those attending the purification of sodium sulfate, provided that isomorphous substances are absent. The mother liquors may be made to yield at least two more crops of crystals; their evaporation for this purpose is free from danger only when the platinum vessels employed are so constructed as to prevent the entrance of carbon dioxide. The yield of pure sodium chromate may be nearly 50 per cent. of the amount corresponding to the pure sodium dichromate employed. Pure sodium chromate must be preserved in a desiccator, containing a small amount of a solution of sodium hydroxide solution to absorb carbon dioxide. If the salt is to be kept for any length of time it should be placed in platinum, gold or quartz vessels. The tetrahydrate is the most convenient form in which to preserve the salt for long periods, as it is permanent under usual conditions.

The Hydrates of Sodium Chromate.

The decahydrate, $Na_2CrO_4.10H_2O$, isomorphous with common Glauber's salt, is so well known that description is unnecessary. It is easily obtained in large crystals by inoculating a cold supersaturated solution of the former salt with a crystal of the latter. In order to avoid the suspicion of contamination with sulfate, inoculation was carried out successively on several watch glasses, the first being touched with sulfate, the second with chromate taken from the opposit side of the first and so on, the bulk of the material being inoculated with pure chromate from the last watch glass. Whenever the temperature of the laboratory had r sen above 20° this procedure was necessary, because at this temperature all of the chromate in the laboratory suffered change into the tetra- or hexahydrate, and so none remained wherewith to start the crystallization of a new specimen. Like sodium sulfate, the chromate has a wide range of metastability of supersaturation, and like it, the chromate is efflorescent in the dry air of the steam-heated[1] laboratory. In order to make sure of the composition of the salt, a specimen which had been dried as much as possible without visible efflorescence was analyzed. 0.8316 gram of the salt lost on dehydration 0.4358 gram of water, or 52.43 per cent. The theoretical percentage is 52.70, hence there can be no doubt as to the formula $Na_2CrO_4.10H_2O$.[2]

[1] Kopp's ascribing deliquescence to the salt must have been due to his working in a very moist atmosphere.

[2] These analyses, as well as those of the hexa- and tetrahydrate given further on, were kindly made by J. B. Churchill under the direction of one of us.

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The hexahydrate, $Na_2CrO_4.6H_2O$, has only a very small range of stability, as will be seen from an examination of the diagram on p. 854. The preparation of this hydrate was first described by Salkowski.[1] At temperatures below 19.53°, especially in contact with its solution, it tends to pass into the decahydrate modification and above 26°, into the tetrahydrate. Inasmuch as the temperatures within which it is stable are those most frequently found in the laboratory, it is the phase most frequently met with. When the decahydrate warms to 19.53° or the tetrahydrate cools to 26° particles of hexahydrate in the atmosphere induce the crystallization of this form so readily that it is often difficult to prevent the appearance of this phase. In two analyses, 1.4152 grams and 1.7786 grams of the salt lost respectively 0.5705 gram and 0.7122 gram of water on drying at 180° to constant weight. These results correspond to 40.3 and 39.4 per cent. of water respectively, and since the first sample was somewhat moist and the second was slightly effloresced, there can be no doubt that the substance was really $Na_2CrO_4.6H_2O$, a salt possessing theoretically 40.0 per cent. of water. The material gives a transition point at about 25.9° (hydrogen scale), being converted into tetrahydrate at that temperature.

The tetrahydrate, $Na_2CrO_4.4H_2O$, is stable in contact with its solution only at temperatures above 26° and below 62.8° ±. Even in the dry air of a steam-heated room it shows no evidence of efflorescence; therefore its aqueous vapor pressure must be very low. This hydrate is formed when a hot concentrated solution of sodium chromate is allowed to cool to a temperature above 26°, and the needle-shaped crystals melt at about 62.8°. Occasionally other crystals of a hydrate or anhydride separate from the solution above 62.8°. Because the hydration of the latter crystals at low temperatures is slow, enough water should be added to a very hot solution to keep the salt dissolved until the temperature 62.8° has been reached by the cooling material. Two analyses of the tetrahydrate showed 30.74 and 30.76 per cent. of water, sufficiently close to the theoretical value 30.72. On cooling a solution saturated at 63°, it frequently happens that no crystals appear, although upon adding a crystal of the tetrahydrate crystallization at once occurs.

In the accompanying figure the solubilities[2] of sodium chromate in contact with its various hydrates have been plotted for temperatures in the neighborhood of the room temperature. Evidently three transitions are possible within a small range. The decahydrate undergoes transition to the hexahydrate and solution at 19.53°, or into tetrahydrate and

[1] Salkowski, *Ber.*, 34, 1947 (1901). The salt had been made and analyzed previously by Richards and Churchill, but no description had been published.

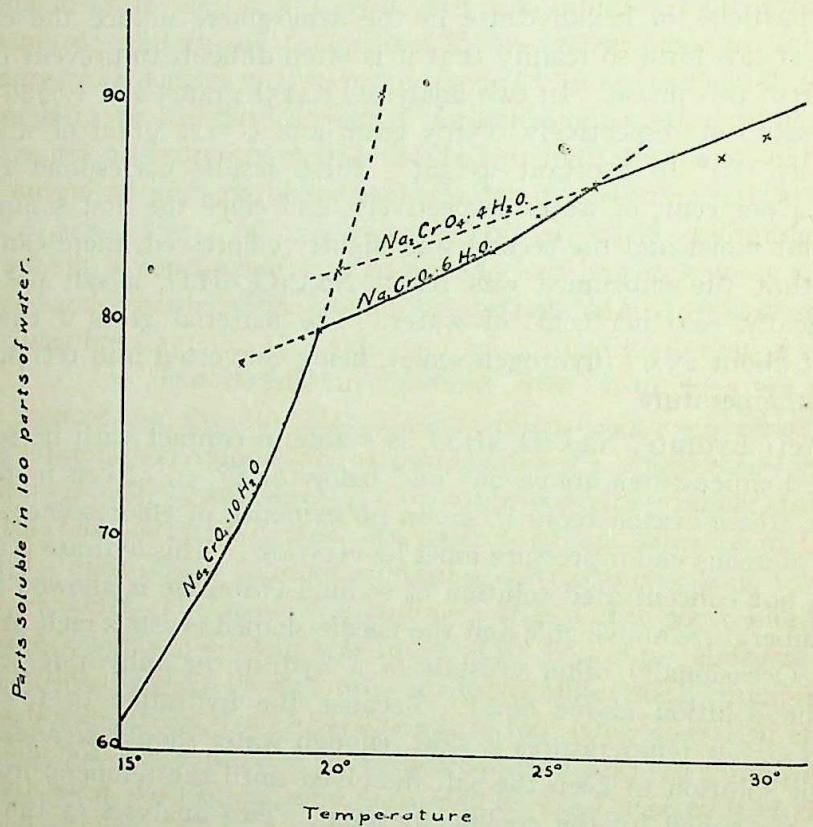
[2] Mylius and Funk, *Ber.*, 33, 3688 (1901); also Salkowski, *Ibid.*, 34, 1948 (1901). These are recorded in *Landolt-Börnstein Tabellen* (1905), page 557.

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solution at 19.99°,[1] depending on which of these last-named hydrates is present. A similar transition from hexahydrate to tetrahydrate and solution occurs at 25.9° ±.

To bring about the transition at 19.99°, it is necessary to superheat the decahydrate past the lower transition point, 19.53°. Not many other instances of this sort have been carefully studied. Walker and Fyffe[2] have examined the solubility of $Ba(C_2H_3O_2)_2.3H_2O$ (which undergoes



a transition into the monohydrate and solution at 24.7°) as far as 26.1°, 1.4° above its transition point; and the solubility of $\alpha Ni(IO_3)_2.2H_2O$ has been studied by Meusser[3] up to 50°, 13° above the temperature of its transition into the anhydride and solution.[4]

The addition of a foreign substance not isomorphous with the deka-hydrate lowers the transition point as usual.[5] The addition of sodium chloride was found some time since by C. A. Bigelow and one of us to lower

[1] This is probably the point found by J. L. R. Morgan as approximately 19.92, *Z. anorg. Chem.*, 55, 263 (1907).

[2] Walker and Fyffe, *J. Chem. Soc.*, 83, 180 (1903).

[3] Meusser, *Ber.*, 34, 2440 (1901).

[4] See also Berthoud, "Sur l'impossibilité de surchauffer un solide," *J. chim. phys.*, 8, 337 (1910).

[5] Löwenherz, *Z. physik. Chem.*, 4, 349 (1889).

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the transition temperature (19.53) about the expected amount. This result was not published at the time, but has since been confirmed by J. L. R. Morgan.[1]

A much more interesting effect is observed with isomorphous hydrates. For example, successive additions of sodium sulfate to the solution gave successive elevations of the transition temperature, even when the crystals contained no sodium sulfate.[2] These elevations were roughly proportional to the amount added. The experiments were not carried on with a view to determining the limits of this change, but an elevation of about 4° was found in some instances. The temperatures at first obtained were variable, but on vigorously stirring in an environment 0.5° warmer than the mixed hydrates, equilibrium was apparently reached after five minutes, and often remained undisturbed for fifteen minutes or longer. This raising of the transition point involves an interesting extension of the range of stability of the decahydrate.

So far as we can find this phenomenon of the raising of the transition temperature of hydrated crystals by the presence of isomorphous hydrated crystals is here described for the first time. It deserves and shall receive here in the near future more thorough investigation.

The relative composition of crystals and mother liquor seemed worthy of study. A solution of sodium chromate containing a considerable amount of sodium sulfate was cooled to 10° to crystallize. The crystals were drained in a centrifuge, washed with a little cold water, and again centrifuged. 7.05 grams of this solution contained 0.432 gram of sodium sulfate and 1.707 grams of the chromate, whereas 2.25 grams of the hydrated crystals contained 0.425 gram of the sulfate and 0.515 gram of the chromate. The solubility of the chromate at 10° is, roughly speaking, 50 parts in 100 of water and of the sulfate 9 parts in 100 of water. The distribution of the dissolved substances between their solution and mixed crystals is thus seen to be in the same sense as to their respective solubilities at the temperature of crystallization. The sulfate decidedly tends towards the crystals, the chromate towards the mother liquors.

As has been elsewhere pointed out, Salkowski was the first to observe that the curve of solubility of the hexahydrate cuts those of the deca- and tetrahydrates at about 19.5° and 26° respectively. Mylius and Funk[3] earlier observed that the transition from the decahydrate is accomplished through the intermediate tetrahydrate, which is stable between 20°

[1] Morgan, *Z. anorg. Chem.*, **55**, 263 (1907); 56, 168 (1907).

[2] This fact was first observed by Churchill and one of us over ten years ago, but has not been published until now. The value 19.6° (which made no pretensions to great accuracy) assigned at that time to the lowest transition temperature of sodium chromate was undoubtedly too high from this cause. *Proc. Am. Acad.*, 34, 277 (1899).

[3] *Abhandlung der Physik. Techn. Reichsanstalt*, 3, 449 (1900). This fact had also been observed but not published by Richards and Churchill before that time.

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and 65°. Salkowski,[1] commenting upon their work in view of his later discovery of the hexahydrate, says that this statement must be extended to include the hexahydrate for its few degrees of stability. The statement of Salkowski must now be extended to include the fact that the transition from decahydrate to the anhydride may be through the hexa- and tetrahydrates, or in the absence of the hexahydrate, this transition may be through the tetrahydrate alone, as originally stated by Mylius and Funk.

We have confirmed the statement of Salkowski that the température of the transition from the hexahydrate to the tetrahydrate is in the neighborhood of 26°, but owing to lack of time we have been unable to determin this point with exactness.

The exact determination of the two lower transition points, for use in precise thermometry, will now be described.

The Apparatus.

The apparatus employed was like that employed in determining the transition temperature of sodium sulfate.[2] It was essentially similar to Beckmann's well-known freezing-point apparatus, consisting of two large test tubes, one within the other, immersed for nine-tenths of their length in a roomy, transparent water bath. The inner test tube, which contained the mixed hydrate, was 3.3 cm. wide and 16 cm. long (internal measurements) and had a capacity of 120 cc. The outer tube was large enough to allow a small air space between the two vessels at every point except the top, where the inner vessel was insulated from the outer one by a narrow rubber ring. This ring held the inner tube in place, preventing heat conductance through the glass to the material, and excluded the outer air from the space between the two tubes. Thus all the heat obtained by the melting material come to it from the outer bath through the confined air-jacket, which is an absolutely necessary provision, if accuracy is sought.

The inner large test-tube containing the sodium chromate was closed at the top by a rubber stopper, carefully freed from loosely adhering matter which might contaminate the materials. It was pierced by two holes, through which short glass tubes were passed. One of these tubes was of the same length as the thickness of the stopper, and served to hold the stirrer; while the other reached 0.7 cm. above the stopper and below to within 1 cm. of the sodium chromate, and served to admit and support the thermometer. To the upper end of the latter tube a short length of stout rubber tubing was attached, the object of which was to hold the thermometer in place at any desired level. A water jacket

[1] *Loc. cit.*

[2] Richards and Wells, *Z. physik. Chem.*, 43, 465 (1903); *Proc Am. Acad.*, 38, 43 (1902).

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around the thermometer is necessary only where the temperature of the room is several degrees distant from 20°, because a correction for the protruding column can be applied with sufficient accuracy when the temperature difference is small.

The stirrer was made of a piece of platinum wire 15 cm. in length, at one end bent into the shape of a ring, at the other end sealed into a glass tube which served as a handle.

The thermometers were three in number. The first, an excellent Beckmann thermometer, the scale of which was divided into hundredths of a degree, was used for the preliminary experiments, where the constancy of the transition temperature of successive fractions was the main issue. Two Baudin thermometers, 15200 and 15276, standardized with the greatest care at the Bureau Internationale des Poids et Mesures, were used in the final determination of the points on the hydrogen scale. These thermometers have been previously described;[1] their scales are divided into tenths of a degree, and readings within 0.001° were made by means of a Geneva cathetometer, observing the marks not only in the usual way, but also through the glass behind the mercury. The freezing points were taken both before and not long after the transition temperatures, and during the intervening time the instruments were carefully protected from large temperature changes.

The Temperature of the Transition from $Na_2CrO_4.10H_2O$ to $Na_2CrO_4.6H_2O$.

When moist crystals of the decahydrate are melted without the addition of the solid hexahydrate, the temperatures obtained are variable and generally low. This is undoubtedly due to the fact that the water of crystallization, together with the water adhering to the crystals, is enough to dissolve the sodium chromate completely, thus preventing the formation of solid hexahydrate.

In order to avoid this difficulty, it was found best to heat about one-fifth of the moist hexahydrate in a quartz or platinum vessel to 60°, thus driving off perhaps a third of the water of crystallization. The cooled product yielded solid $Na_2CrO_4.4H_2O$ and its solution. This was added to the remainder of the $Na_2CrO_4.10H_2O$, after which the whole mass was warmed to 28° C in the test tube in which the determination was to be made. The proportion of $Na_2CrO_4.4H_2O$ to $Na_2CrO_4.10H_2O$ should be such that at this temperature the whole is in solution. The solution was then cooled by dipping the test tube into a beaker containing water at twenty degrees. When the temperature of the solution had fallen to 25°, a crystal of $Na_2CrO_4.6H_2O$ was added; it produced copious crystallization. On further cooling to 18° or slightly lower a crystal of decahydrate was added, and still more heat was taken from the mixture,

[1] Richards and Wells, *Proc. Am. Acad.*, 38, 43 (1902); *Z. physik. Chem.*, 43, 465 (1902)

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with stirring, until the mixture of the two solid phases and solution of sodium chromate was plastic.

The temperature of the water bath was kept one or two tenths of a degree higher than the equilibrium point (19.5°) and the room temperature also was kept not far away. This latter condition was not very essential, because with one of our thermometers the stem exposure was 6.5° and with the other only 0.5°.

In a preliminary set of readings, corrected in the usual way for calibration, for internal and external pressure, for error in the fundamental interval, for the corrected ice point, for the exposed column, and to the hydrogen scale, the following values were found:

Preliminary determination by thermometer 15200	19.518°
Preliminary determination by thermometer 15276	19.525°
	19.522°

The Beckmann thermometer in this mixture indicated 0.580°. Upon crystallizing the material once more, and separating the mother liquor by centrifugal action, the crystals still gave exactly the same transition point, 0.580°, the atmospheric pressure having remained essentially constant. Therefore it was clear that the material was as pure as it could be obtained by crystallization, and the final estimation was made.

The individual readings were corrected for stem exposure, and all averaged to give the observed value used in calculating the temperature referred to the hydrogen scale. The ice points, which are the most uncertain part of this determination, were taken as the averages of four separate fairly concordant sets of readings, two of which were made some time before the determinations, and two immediately afterwards. As the thermometers are old and well-seasoned, this procedure seemed likely to furnish the best results.

Thermometer 15200:

Reading in salt (cor.)	19.804°	In ice	+0.201°
Correction, calibration	−0.026		+0.002
Correction, internal pressure	+0.027		+0.009
	19.805°		+0.212°
Corrected reading in ice	−0.212		
	19.593°		
Correction, fundamental interval	+0.014		
	19.607°		
Correction to hydrogen scale	−0.084		
	19.523°		

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Thermometer 15276:

Reading in salt (cor.)	19.750°	In ice	0.143°
Correction, calibration	—0.025		—0.001
Correction, internal pressure	+0.039		+0.012
	19.764°		+0.154°
Corrected reading in ice	—0.154		
	19.610°		
Correction, fundamental interval	+0.001		
	19.611°		
Correction to hydrogen scale	—0.084		
	19.527°		
Total average of two final readings	19.525 ± 0.002°		

The average of the two preliminary readings was 19.522° ± 0.004°, a result as near as could be expected to the final value, considering the range of error of each. The value 19.525°, the result of the final determination above, may be accepted for the present as the most probable figure.

The Temperature of the Transition from $Na_2CrO_4.10H_2O$ to $Na_2CrO_4.4H_2O$.

This mixture of hydrates is somewhat more difficult to prepare than the mixture of deca- and hexahydrates. From a study of the diagram on page 854 it appears that the tetrahydrate is metastable with respect to the hexahydrate between the temperatures 19.53° and 25.9° ±. The difficulty is to exclude the hexahydrate during the cooling of the tetrahydrate and solution from 26° to 19.99°, the transition point of the deca- to the tetrahydrate. Even after the decahydrate has appeared and has in part relieved the supersaturation, care must be taken to exclude the intermediate hydrate. At 19.99° both decahydrate and tetrahydrate are metastable with respect to the hexahydrate. If to a mixture of the two former a crystal of the latter be added, a depression and irregularity in the temperature occurs, and the temperature gradually falls to that of the lower transition point.[1]

The mixture of hydrates is prepared (within the test-tube in which the transition temperature is to be determined) by a method closely resembling

[1] Gernez's supposed disintegration of $Na_2CrO_4.4H_2O$ in the presence of 10 H_2O salt [*Compt. rend.*, 149, 77 (1910)] would not affect this point, as Gernez reasonably supposes this disintegration is due simply to the formation of the decahydrate from included water within the salt, and not to the formation of a hydrate with less than 4 H_2O.

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that described for preparing the mixture of decahydrate and hexahydrate. To the decahydrate is added such a quantity of tetrahydrate that nearly all the solid will be in solution at 28°. By heating the mixture to this temperature, one may feel certain that none of the hexahydrate is present. The tube is then closed by a clean stopper through which the handle of a stirrer passes. The stopper serves to protect the contents from accidental inoculation by hexahydrate. When the solution has been cooled to about 19°, it is inoculated with some freshly prepared decahydrate, which must be free from hexahydrate. Further gradual subtraction of heat, with constant stirring, gives a mixture of the desired plastic consistency.

The material used in the preliminary determination of this transition point was the same as that used in the preliminary determination of the equilibrium temperature of the mixed deca- and hexahydrates. With the Beckmann thermometer the new point was 1.039°. On the Baudin thermometers all individual readings were corrected for stem exposure and averaged as before.

Preliminary reading by thermometer, 15200	19.984°
Preliminary reading by thermometer, 15276	19.990°
Average,	19.987°

The material used in the final observations was the same as that used for the previous final work, after conversion into a mixture of deca- and tetrahydrate. With the Beckmann thermometer it gave the transition point 1.039, the same as that given by the salt used in the preliminary tests just recorded.

FINAL DETERMINATION I.

Thermometer 15200:

Reading in salt (cor.)	20.269°	In ice	0.201°
Correction, calibration	−0.028		+0.002
Correction, internal pressure	+0.027		+0.009
	20.268°		0.212°
Corrected reading in ice	−0.212		
	20.056°		
Correction, fundamental interval	+0.014		
	20.070°		
Correction to hydrogen scale	−0.085		
	19.985°		

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FINAL DETERMINATION II.

Thermometer 15276:

Reading in salt (cor.)	20.209°	in ice	0.143°
Correction, calibration	—0.022		—0.001
Correction, internal pressure	+0.039		+0.012
	20.226°		0.154°
Corrected reading, in ice	—0.154		
	20.072°		
Correction, fundamental interval	+0.001		
	20.073°		
Correction to hydrogen scale	—0.085		
	19.988°		
Total average of two final readings	19.987° ± 0.002		

It is interesting to note that the difference between the two transition temperatures is given as almost exactly the same quantity by the final readings of the two thermometers.

Difference by thermometer 15200 = 0.462°
Difference by thermometer 15276 = 0.461°

This, of course, gives a means of calibrating the Beckmann thermometer, which gave 0.459° for the interval—evidently the marks were a trifle too far apart on the latter instrument.

The close parallelism of the results with the two Baudin thermometers seems to indicate that the most probable cause of error in such work is not due to mistakes in observing either of the transition temperatures, but rather to the difficulty of determining the ice point. There can be no question that either of the sodium chromate equilibrium temperatures is a far better means of fixing the scale of a thermometer to be used near room temperature than is the freezing point of water.

The Temperature of the Transition from $Na_2CrO_4.6H_2O$ to $Na_2CrO_4.4H_2O$.

The material used in this determination was sodium chromate obtained from the mother liquors of previous preparations, purified by recrystallization as decahydrate until the temperature of transition from the decahydrate to the hexahydrate as shown by the Beckmann thermometer was 0.580. A supersaturated solution of this pure salt at 25° was inoculated with hexahydrate and further cooled with stirring to 18°, the decahydrate being scrupulously excluded. The plentiful crystals of hexahydrate were then centrifuged to remove the excess of mother liquor, and in order to make certain that none of the decahydrate was present, the crystals were allowed to stand in a bath at 25° for an hour. No change occurred in the appearance of the material. Just before taking the transition temperature a few crystals of the tetrahydrate were added.

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Whether on account of the interference of other unknown hydrates, or of the comparatively small heat of this transition, or of the unavoidable haste in which the experiments had to be conducted, much less constant results were obtained in this case than in the preceding. It appeared that the equilibrium temperature of the hexa- and tetrahydrates was not far from 25.90° on the hydrogen scale; but this figure is subject to further revision.

This point is worthy of further investigation, for it is exceedingly convenient, taken together with the other points given by this same salt, as a means of calibrating a Beckmann thermometer. The interval between the decahydrate-tetrahydrate point (19.987°) and the higher transition temperature is almost 6°, the usual length of a Beckmann thermometer. By adding a degree to the scale, which could easily be done in future, the lowest transition temperature of sodium chromate could be brought within the scope of the instrument. To be able to verify a thermometer over its whole length, and at the same time to evaluate accurately the interval 0.462 on one part of the scale, all with the single purified salt, is indeed a highly desirable circumstance.

Of course the determination of all the three points as given in this paper must be looked upon as merely preliminary, because time permitted the study of these temperatures on only two thermometers. The average of the readings of many thermometers should ultimately be taken. Nevertheless we believe that the averages given in this paper are sufficiently exact to be a great boon to those desiring to verify thermometers about the temperature of the room.

It is a pleasure to acknowledge the usefulness of a grant made many years ago by the Rumford Fund of the American Academy of Arts and Sciences for this purpose. Much of the material used in the investigation was purchased with its aid.

Summary.

1. The great advantage of sodium chromate as a means of verifying thermometers at three fixed temperatures in the neighborhood of 20° is emphasized.

2. A method for the easy preparation of pure sodium chromate has been elaborated.

3. The existence of three hydrates of sodium chromate, namely, the deca-, hexa- and tetrahydrates has been confirmed.

4. The accurate estimation of the point of conversion of each of these hydrates into each of the other two has been shown to be easily feasible.

5. The addition of heteromorphous substances lowers the transition points as usual.

6. The addition of sodium sulfate (which gives an isomorphous decahydrate) raises the temperature of the decahydrate-hexahydrate equilib-

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rium. This is perhaps the first observation of this type of phenomenon.

7. The temperature of the decahydrate-hexahydrate transition is found to be approximately 19.525°, on the international hydrogen scale.

8. The temperature of the decahydrate-tetrahydrate transition is found to be approximately 19.987 on this scale.

9. The temperature of the hexahydrate-tetrahydrate transition is found to be approximately 25.90°, on this scale.

10. All these points, especially the last, are to receive further investigation at Harvard in the near future.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]
INVESTIGATIONS ON LIGHT AND HEAT PUBLISHED WITH AID FROM THE RUMFORD FUND.

A METHOD FOR DETERMINING HEAT OF EVAPORATION AS APPLIED TO WATER.

BY THEODORE W. RICHARDS AND J. HOWARD MATHEWS.

Received April 8, 1911.

Among usual calorimetric measurements none has been in the past less satisfactory than the measurement of heat of vaporization. The methods employed have been almost as untrustworthy as they have been numerous. The results for water are indeed not very divergent, but in most other cases there is little or no concordance. In the case of ethyl formate, for example, the variation in the values given by different experimenters is over 10 per cent.; in the case of ethyl acetate, the extreme difference is over 13 per cent. These cases have been selected because they concern substances carefully investigated by many observers; less carefully studied cases might have been selected which show even greater discrepancies. Evidently most of the results are in error: but which are the correct ones? The newest values are by no means necessarily the best, for wide discrepancies have appeared in the most recent work. Part of the errors were undoubtedly due to impurity in the materials, and some to faults in the methods.

Desiring really to know the heats of evaporation of a few liquids, we felt hopeless concerning our ability to select among these discordant figures. New research was evidently needed, involving great care in purification of material, and careful choice of the best details of experimentation. The present paper contains an account of the evolution of a satisfactory method.

A brief account of previous methods may well precede the description of our own experimental work, as this was based partly on the successes and partly on the failures of others.

The methods used for measurements of heats of evaporation are of two classes. In one the energy used in the process of vaporization is

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measured; in the other the energy given up by the condensation of vapor is evaluated; each procedure should of course yield the same results. Most of the methods used, particularly the earlier ones, belong to the latter class; because, although those belonging to the first class have the advantage of being independent of the values for the specific heats of the substances used, they are more complicated in manipulation and calculation, and none has proved to be entirely satisfactory.

Joseph Black[1] was the first to make the interesting observation, that in the formation of the vapor phase from the liquid phase heat is absorbed. His first experiments, though extremely crude, were sufficient to show that in the case of water the amount of heat absorbed by this transformation is considerable. Somwhat later Black and Irvin made further experiments in this direction, and found the value 520 calories per gram, which is surprizingly close to the now generally accepted value, considering the crude method with which they worked. In 1781 Watt[2] for a short time attacked the subject at the suggestion of Black, and about fifteen years later returned to it and made a number of measurements, the details and results of which he published. He pointed out that heat is lost through radiation, but found no method of measuring this loss. He showed also that the condenser gains heat by conduction when connected directly to the boiler by means of a metallic tube, and sought to overcome this source of error through making the connection by means of a cork, so that metallic contact was avoided. The average of eleven separate determinations gave him the value 525.2 calories, or 625.2 from zero,[3] the values varying from 612.9 to 637.1, a difference of about four per cent.; but he expressed his opinion that the true value is not far from 633 calories.

Somewhat later Count Rumford[4] made three experiments concerning the same constant, finding the mean value 667 as the total heat of evaporation from zero—a result much higher than Watts'. Rumford also determined the heat of evaporation of two or three organic liquids, but these results have no value, since, as he admits, the substances were not pure. In this work he sought to overcome the error due to radiation by starting a determination with the calorimeter water at a temperature as much below the surrounding temperature as it would be above it at the completion of the determination, on the assumption that the gain in heat during the first half of the total time would be exactly counterbalanced by the loss in the second half. This practice has

[1] See Regnault's Experiences, Part I, p. 635 (1847).

[2] Regnault, *Mém. de l'Inst. de France*, 21, 635 (1847); Robinson's, *Mechanical Philosophy*, 2, 5 (1822).

[3] This latter number includes the heat necessary to raise the gram of water from 0° to 100°.

[4] See Biot's, *Traité de Physique*, 4, p. 710.

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recently been found to be of very doubtful advantage.[1] In 1818 Ure[2] found the value 637.5 calories; and Despretz,[3] in 1823, published the value 631 as the result of one series of measurements, and 640 as the result of a second series, his apparatus having been similar to that used by Rumford. The next work was done by Brix[4] in 1842, who pointed out many of the causes of error and sought to correct them mathematically. His value for water was 640, including the heat given up by the water between 100° and 0°—a result very close to the most probable figure.

In 1847 Regnault[5] published his exhaustive memoir upon this subject, which surpassed in detailed precaution any preceding work. As an average of 38 separate determinations he obtained the value 636.67 calories, the individual values varying between 635.6 and 638.4.

The work of Andrews[6] may be considered somewhat more in detail, because his method was similar to those which have since been usually employed. He distilled the liquid from a screened retort into a spiral condenser placed in a calorimeter, and noted the rise in temperature. The water equivalent of his calorimeter, water, and utensils was only about 280 grams, the amount of water distilled was a little less than two grams, and there was no device to prevent particles of water from being carried over in the vapor, so that the method was still evidently in its infancy. His thermometric precautions and his efforts to apply corrections for heat lost and gained by radiation were very crude, as was also his method for determining specific heats; but nevertheless, for alcohol, he obtained 202.4 at the boiling point, a value which is but 3 per cent. lower than the present accepted value. His two figures for water, 531 and 543 calories (not including the heat required to warm the water), obtained at different rates, were less satisfactory; premature condensation evidently took place in his apparatus.

Favre and Silbermann[7] shortly afterwards measured th heats of vaporization of a number of organic liquids as well as of water, but the amount of material used was very small and the method in general unsatisfactory, so that their results are of but doubtful value.

The next work of importance is that of Berthelot,[8] whose method (a modification of Andrews') is so well known as to need no description. The vaporizer was placed immediately over the calorimeter and heated by a ring burner, the tube for delivering the vapor passing through

[1] T. W. Richards and L. L. Burgess, THIS JOURNAL, 32, 449 (1910).
[2] Ure, *Phil. Trans.*, 1818, 385.
[3] Despretz, *Ann. chim. phys.*, [2] 24, 323 (1823).
[4] Brix, *Pogg. Ann.*, 55, 341 (1842).
[5] Regnault, *Mém de l'Inst. de France*, 21, 638.
[6] Andrews, *Pogg. Ann.*, 75, 501 (1848).
[7] Favre and Silbermann, *Ann. chim. phys.*, [3] 37, 461 (1853).
[8] Berthelot, *C. R.*, 85, 646.

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the ring. His apparatus, although ingenious, has grave defects, some of which have been pointed out by Schiff[1] and by Kahlenberg.[2] Superheating of the vapor, the most glaring defect, was suspected by the former critic, but the experimental demonstration was first made by the latter. Another source of error is direct radiation from the burner into the calorimeter, for which, however, an approximate although unsatisfactory correction may be applied. There was no device to prevent the vapor which came off from the liquid before it reached the boiling point from gaining access to the condenser.

Passing over the work of Schall,[3] who used the method of Favre and Silbermann, we come to the work of Robert Schiff,[4] who sought to avoid the causes for error in the Berthelot apparatus by removing the source of heat from the neighborhood of the calorimeter, and interposing a small silver trap just before the entrance of the vapor into the condenser. By this ingenious device, particles of unvaporized material that might be carried over by the current of vapor, and most of the liquid resulting from a premature condensation of the vapor, would be caught and prevented from going into the condenser. Some of the earlier experimenters had sought to prevent prematurely condensed liquid from reaching the condenser by making a sharp bend in the vapor delivery tube, so that condensed liquid would run back into the vaporizer, but Schiff's device has the decided advantage that the trap can be placed much closer to the condenser, so that the amount of condensation between this point and the condenser will be smaller. That this was a distinct imp ovement is apparent in his results; they were among the best that have been made. While the method of Schiff is undoubtedly better than any similar methods previously used, it is objectionable in the case of liquids of higher boiling point, as Kahlenberg has shown. The danger here arises from the fact that a substance of high boiling point condenses in the trap to such an extent that it finally overflows and runs into the condenser.

Another objection, heretofore not mentioned, lies in the fact that the vapor, just before it reaches the calorimeter, passes through a zone, which, though heated, is not quite as high in temperature as the boiling point, and consequently premature condensation is not wholly avoided. By no means all of the heat thus lost finds its way into the calorimeter. The result of this defect is to give a value lower than the true heat of vaporization.

In the hands of Louguinine[5] the apparatus of Schiff has been so perfected as to make it one of the most satisfactory heretofore used. The

[1] Schiff, *Ann.*, 234, 338 (1886).
[2] Kahlenberg, *J. Physic. Chem.*, 5, 215 (1895).
[3] Schall, *Ber.*, 17, 2199 (1884).
[4] Schiff, *Loc. cit.*
[5] *Ann. chim. phys.*, [7] 7, 251 (1896).

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tube leading to the trap was made large in order to prevent the clogging with condensed liquid. The proximity of the hot trap to the calorimeter necessitated a correction for heat gained therefrom through radiation and conduction. In Schiff's work this correction appears to have been omitted, but Louguinine evaluated this cause of error by keeping the trap hot while he prevented both vapor and liquid from entering the condenser. In this way the heat gained per minute by radiation and conduction can be determined fairly well, and, knowing the time during which vapor enters the condenser and gives up heat, a suitable correction can be made for the heat gained by radiation and conduction during the same period. Louguinine made the distance from the trap to the condenser very short (15 mm.) in order to reduce the premature condensation of the vapor, but our experience indicates that even then he could not have been wholly successful. The fact that his results for the heat of vaporization of water are fairly concordant does not prove the absence of error from this cause. To reduce condensation to zero, the distance between trap and condenser should also be reduced to zero—an obvious impossibility. Because, as has been said, the effect of the error is to make the heat of vaporization appear less than it really is, Louguinine's three values, 535.61, 537.61 and 538.51 calories per gram, are probably too low.

About fourteen years ago J. A. Harker[1] published an elaborate and interesting account of his work. His early rejected experiments demonstrated more conclusively than ever the danger of premature condensation, and he concluded that this cause of error is inevitable, when the vapor is introduced from above. In his later work, fearing that minute drops of water exist in vapor as ordinarily formed in distillation, he passed the vapor through coils in a heated oven, and then through a zone kept at a constant temperature about three degrees above the boiling point. Finally the vapor was admitted into the condensing coil of the calorimeter, through the side of the latter, the temperature being taken at the point of introduction by means of a calibrated thermo-couple. The apparatus was ingenious, but the conduction of heat into the calorimeter from the entering tube must have been considerable, and heat was undoubtedly gained also by direct radiation from the black interior surface of the ebonite chamber at the opening in the side of the calorimeter.

He concluded from his experiments, which he wished to be considered as merely preliminary, that the true value for the heat of vaporization of water (not including the heat given out in cooling the water) is about 540 calories. Unfortunately, his data, corrections and calculations are not given.

Kahlenberg,[2] in an almost simultaneous investigation, sought to re-

[1] Mem. Manchester, *Lit. and Phil. Soc.*, [4] 10, 38 (1896).

[2] Kahlenberg, *J. Physic. Chem.*, 5, 215 (1895).

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tain all the good qualities of the method of Berthelot, and at the same time endeavored to eliminate its sources of error by an ingenious modification, using the heat generated from an electric current conveyed by a resistance wire immersed under the liquid to be vaporized, in order to produce the vaporization. Thus superheating is avoided, as well as the presence of any flame near the calorimeter. This method, undoubtedly one of the best heretofore used, has yielded fairly good results, which are nevertheless undoubtedly somewhat vitiated by premature condensation.

Other methods which should be considered are the electrical methods of Marshall and Griffiths,[1] of Marshall and Ramsay,[2] of Brown,[3] and of Henning.[4]

The method of Marshall and Griffiths is exceedingly complicated, and the heat of vaporization of but one substance, benzene, has been obtained. The values were determined for the temperatures of 50°, 40°, 30° and 20°, and the value at the boiling point obtained by extrapolation. Upon this value for benzene, thus obtained, was based all the work done by Marshall and Ramsay. This latter method was merely a comparative method. The electric current was sent through two similar vaporizers in series, and the amount of liquid distilled from each was weighed. The results obtained all depended, therefore, upon the value of the heat of vaporization of one substance, and for this one substance different experimenters had found values differing by over sixteen per cent. The investigators state that they were unable to obtain any satisfactory results for water, perhaps because of electrolysis and its consequent consumption of electrical energy.

Brown, working with a single apparatus, passed a current of measured value for a measured time through a wire of known resistance, immersed under the liquid. The portion evaporated was weighed; thus all the data for calculating the heat of evaporation were obtained. As in Ramsay's and Marshall's method the liquid must be at the boiling point before the measured current is passed through, but no knowledge of the specific heat of the liquid is necessary. The results obtained by Brown agree well among themselves, but are even higher in value than those obtained by Marshall and Ramsay.

F. Henning[5] used a method similar in principle to that used by Brown, but superior in detail, because greater precautions were taken to provide against possible errors. The original paper must be consulted for

[1] Marshall and Griffiths, *Phil. Mag.*, [5] 41, 1 (1896).
[2] Marshall and Ramsay, *Ibid.*, [5] 41, 38 (1896).
[3] Brown, *J. Chem. Soc.*, 83, 987 (1903).
[4] Henning, *Ann. Physik*, [4] 21, 849 (1906).
[5] *Loc. cit.*

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particulars, most of which do not immediately concern the present investigation. The greatest difficulty in this interesting and painstaking work seems to have been that considerable heat was necessarily carried away by the conducting wires, and there seems to have been no entirely satisfactory method for measuring or calculating this uncertain quantity. As the mean of his determinations made at an average temperature of 100.59°, Henning found the heat of vaporization of a gram (weighed in vacuum) of water to be 538.25 calories at 15°. A number of determinations were made also at reduced pressures, but they do not concern us here.

A modification of this electrical method has been proposed by A. Cameron Smith,[1] who suggested that the electrically heated vaporizer be suspended from one arm of an analytical balance. This apparatus is suitable only for lecture demonstrations; many possible sources of error tend to diminish its accuracy.

Among these many methods, Kahlenberg's modification of Berthelot's seemed to be preferable, partly because of its simplicity, and partly because it retains the advantage of the electrical method of heating while avoiding the disadvantages. Hence we used this method as the basis of our own, seeking to discover and correct any sources of error which might still remain in it.

The Evolution of the Present Apparatus.

One of the most serious causes of error in all calorimetric work is the more or less uncertain correction for cooling. Hence one of the first steps of the present research was the application of the new method of adiabatic calorimetry to the problem.[2] This method, first put into practice about six years ago at Harvard, has since been used successfully in several calorimetric processes, such as the determination of specific heats of neutralization, combustion, and solution. The method consists in warming the

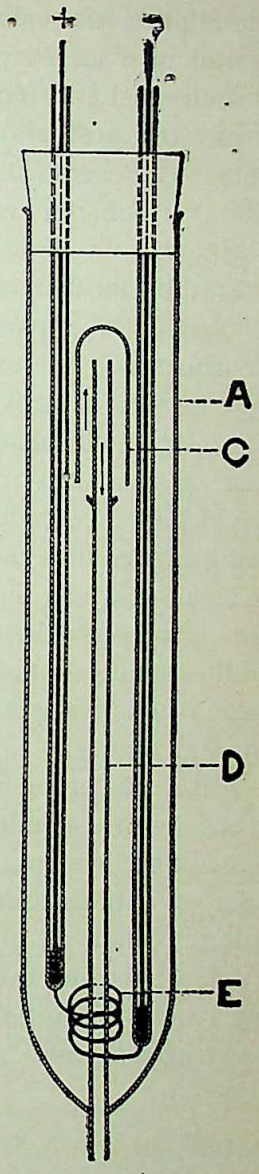


Fig. 1.—First modification of Kahlenberg's vaporizer.

The hood or trap (C) over the delivery tube helps to eliminate mechanically carried drops.

[1] *Proc. Roy. Soc.*, Edinburgh, 24, 450 (1903).

[2] Richards, Forbes and Henderson, *Proc. Am. Acad.*, 41, 1 (1905). See also Richards and Jesse, as well as Richards and Burgess, THIS JOURNAL, 32, 268 (1910) and 32, 431 (1910).

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surroundings of the calorimeter at the same rate and to the same extent as the calorimeter itself during its operation. This is accomplished by surrounding the calorimeter proper by a water-tight jacket, which is immersed in a larger vessel containing dilute alkali. Into the latter can be delivered the requisit amount of acid, the bath being stirred rapidly so as to insure uniformity of temperature. By such a system it is possible to prevent heat exchange to or from the calorimeter proper, and the thermometer is stationary during both the initial and the final readings.

For the measurements of the heat of vaporization a modified form of Kahlenberg's apparatus was combined with the adiabatic method of calorimetry. The exact form of apparatus finally used was reached only by degrees, several successive improvements having been introduced. The first modification of Kahlenberg's vaporizer consisted in the interposition of a trap or hood (C in Figs. 1, 3, 4 and 5) between the boiling liquid and the condenser, to prevent drops of unvaporized material from being carried into the latter by the lively current of vapor. The objection to such a trap as that used by Schiff (namely, premature condensation of vapor) was avoided by keeping the trap entirely enclosed by the vapor of the boiling liquid, and therefore at the same temperature. Furthermore it was made in such a form as to prevent any danger of its filling and running over.

With this apparatus a number of preliminary determinations were made, with a condenser and calorimeter to be described presently, and a striking systematic irregularity was observed in the results. The heat of vaporization of benzene, for example, appeared to be about 89 calories when 25 grams took 14 minutes to evaporate, but as much as 93 calories when the time was shortened to 2.5 minutes, with corresponding results for intervening rates. The results are plotted in the accompanying diagram.

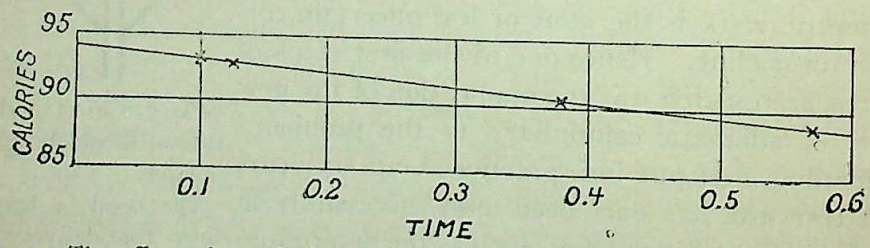


Fig. 2.—The effect of speed of vaporization on the results. (Benzene in the vaporizer shown in Fig. 1.)

In the direction of ordinates are plotted the observed values for the heat of vaporization of a gram of benzol in small calories; in the direction of abscissas are plotted the times (in fractions of a minute) needed for the vaporization of that quantity.

The ordinates represent heats of vaporization in calories, and the abscissas the time in minutes required to vaporize one gram. By a

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comparatively short linear extrapolation we obtain the value 94.1 cal. as the heat of vaporization of benzene. It will be shown in a subsequent paper that this value is very near the most probable value obtained afterwards with better apparatus. Water was found to exhibit precisely the same phenomenon. Previous investigators have not taken into consideration this variation of result produced by varying the rate of distillation, and the oversight undoubtedly accounts for much of the wide variation in the published results.

Consideration of the various possible complications which might bring about this time effect led to the conclusion that it was probably due to premature condensation between the vaporizer and the condensing coil, and the consequent loss of heat from the vapor thus condensed. Evidently such a loss must be directly proportional to the time required for the vapor to pass through the zone of premature condensation. Further, in accordance with Newton's Law of Cooling, the loss of heat should be proportional to the difference in temperature between the boiling point of the substance and the environment of this zone—a conclusion later verified by the facts.

Attempts were next made to eliminate as far as possible the zone of premature condensation. The vaporizer was set into an asbestos shield made n the form of a frustrum of a cone, the space between the asbestos and the glass being closely packed with cotton, and the outside of the cone covered with bright tinfoil to cut down the radiation. In order to place the vaporizer as low as possible and at the same time to prevent its becoming wetted, a shallow glass cup was placed immediately below the asbestos shield. The cup also served to prevent loss of heat by evaporation of the calorimeter water at its surface, or by evaporation of water rising on the vaporizer stem by capillary action or other cause, such evaporation being caused by the presence of the hot tube carrying the vapor. In this manner the distance between the boiling liquid within the vaporizer and the calorimeter water was reduced to a little less than one centimeter.

In spite of the precautions to prevent radiation, the correction for heat gained by the calorimeter due to this cause was increased from about 0.002° to 0.008° per minute, a quantity which was very carefully determined and applied to the results.

This vaporizer yielded results which gave when plotted a line less steep than the previous one. The modification had evidently improved the results, but had not wholly eliminated the cause or causes of error.

In the space above a boiling liquid in a flask, a mist can often be observed. This mist is caused by radiation of heat from the walls of the vessel; and the question arose as to whether the difficulty in obtaining uniform results at various speeds might not be due in part to the for-

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mation of such a mist within the vaporizer. The mist would not be entirely caught by the trap, and would thus introduce minute drops of water into the condenser, possibly proportional in amount to the time required for distillation.

In order to discover whether any difficulty arose from this cause, the vaporizer, above the asbestos cone, was surrounded by a jacket through which live steam was passed throughout the measurement. This must have prevented the formation of a mist within the vaporizer, but the results were no better.

The ejection of fine drops from the surface of the boiling liquid—drops which might be swept along by the current of vapor—could not have been the cause of the particular trouble in question. Such an action would seem more likely when the boiling is rapid than when it is slow, an outcome exactly the opposit to that actually observed. Doubtless such an ejection occurs to a slight extent, but in our trap its effect had undoubtedly been much reduced. As will be seen, our final result shows that we have been at least as fortunate as others in eliminating this danger.

Harker, in his desperation on account of obvious premature condensation, resorted to superheating the vapor, in order to insure its being perfectly dry; accordingly we, too, tested this doubtful device. A coil of fine platinum wire was introduced into our vapor delivery tube, extending nearly its whole length, and a small current was sent through the wire. Several determinations made at different speeds and w th different strengths of current through the co l, gave higher values than before. With a constant strength of current, the slower the speed the higher was the result; and with a constant rate of evaporation, the greater the current the higher was the result. Evidently superheating occurred. With some modifications of the parts and the construction of special thermometers it would have been possible to take the temperature of the vapor as it entered the calorimeter; but the unsatisfactory nature of these experiments offered no temptation to the further prosecution of this line of attack.

Being still convinced that the principal premature condensation took place in the narrow zone between the vaporizer and the condenser, we next sought to reduce further this distance, and to protect the vapor passing through it from loss of heat. A new vaporizer having a vacuum jacket was constructed as shown in Fig. 3, the walls (B) of the jacket being about one centimeter from the walls (A) of the vaporizer, save at the bottom where the distance was about eight millimeters. Both the outer wall of the vaporizer and the inner wall of the jacket were brightly silvered to a distance of about five centimeters above the vapor exit. The vaporizer was set so low that the level (F) of the calorimeter water

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came up on its jacket to a height of a few millimeters. This brought the boiling liquid in the vaporizer to within one centimeter of the calorimeter water, largely protected the vapor from condensation in this zone, and prevented most of the evaporation from the surface of the calorimeter water at the line of immersion. The vaporizer projected a short distance through the adiabatic cover, and, since the projecting part was silvered, the amount of radiation was not excessively large. The space around the vaporizer was closely packed with cotton. With this apparatus, values were obtained which were slightly higher than those previously obtained with the earlier forms of apparatus, when made at the same rate; but they were not as consistent as desired, partly because of the fact that the diameter of the exit of the delivery tube was much too large.

Another attempt to reach a better result led to the cutting off of still more of the delivery tube below, the thermal protection being provided only by a rubber cup, cut from a child's ball, placed between the vaporizer and condenser. The rubber cup was packed with cotton, as was also the space around the vaporizer. After a few determinations, however, the apparatus was discarded, because the correction for radiation and conduction was very large (0.040° per minute), and also because of the difficulty in making a tight joint.

The form of apparatus finally adopted combined all the advantages of the preceding forms, and is shown in Fig. 4. The boiling liquid was surrounded by a vacuum jacket whose walls were about one centimeter from the walls of the boiling compartment, save at the bottom where the space was five millimeters across. In addition to the hood covering the upper end of the vapor delivery tube, the tube was also provided with another trap to catch and retain any liquid that might in any way gain access thereto. This trap

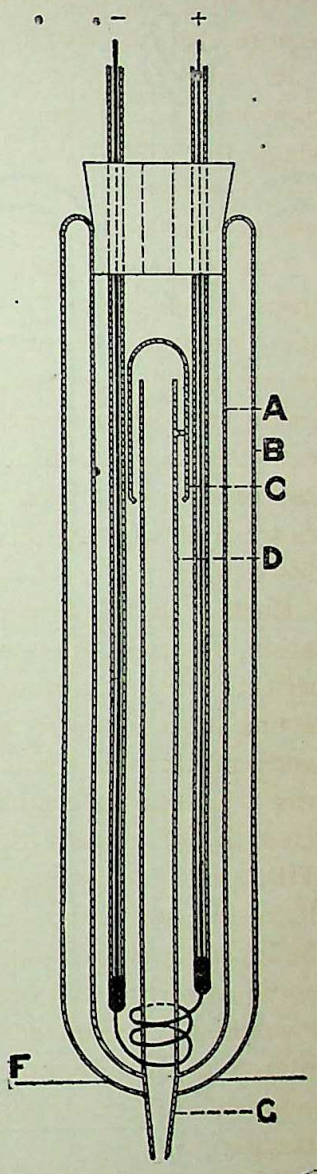


Fig. 3.—A further modification of Kahlenberg's vaporizer. The compartment containing the liquid and coiled platinum wire for heating is surrounded by a silvered vacuum jacket (AB). The trap (C) is retained. The condenser is attached at G. The vaporizer is immersed in the water of the calorimeter as far as the water-line at F.

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was placed as low as possible so that the distance between it and the condenser might be reduced to a minimum, yet it was surrounded by the boiling liquid in order to prevent condensation within it. The heating coil was placed so low as to make sure that the liquid surrounding the trap was at the boiling point. If prematurely condensed liquid now gains access to the condenser, it must come entirely from condensation in the short distance between the trap and the calorimeter water, —because all previously condensed liquid was caught in the trap. After an experiment the trap usually contained a few drops of liquid, sufficient to have introduced appreciable error, had it been allowed to reach the condenser.

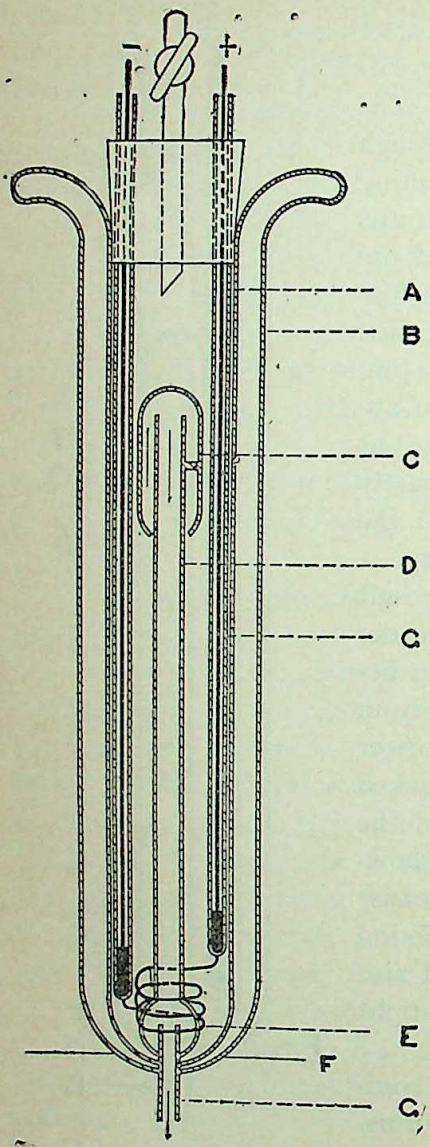


Fig. 4.—Final form of vaporizer (½ actual size).

A vacuum jacket (AB), silvered inside, surrounds the hot vessel, which is provided with a stopcock above. The delivery tube has two traps, one over its top (C), and another (E) as near as possible to the water of the calorimeter below. The condenser is attached at the very bottom at G, and F is the water-line, as in Fig. 3.

The interior of the vacuum jacket was brightly silvered to a height of 4 or 5 centimeters, the silvering being on both walls, so that any heat passing from the boiling liquid to the calorimeter water by radiation had to pass through two brightly silvered surfaces and a vacuum space. The conduction of heat to the calorimeter through the glass itself cannot be prevented, but was made small by having the glass as light as was consistent with the strength demanded. The proper correction was always applied for heat gained by the calorimeter in these two ways, the necessary observations being always determined before each measurement of latent heat. For several minutes previous to admitting the vapor into the condenser, readings of the temperature were made at intervals of one minute, until the increase became constant and of certain value. The nature of the problem is such as to make this correction absolutely necessary, for the vaporizer must be brought close to the calorimeter water,

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and radiation and conduction across this small distance cannot be prevented.

After many experiments had been made, not only with water but also with higher-boiling substances, the accidental cracking of the vaporizer jacket near the top destroyed its high vacuum; nevertheless the correction for the combined radiation and conduction was then found to be but little greater than before. Apparently the two brightly silvered surfaces effectually prevented radiation.

The heating coil had a resistance of about 0.7 ohm, and was supplied with a suitably controlled current of from twelve to eighteen amperes from eight large storage cells. The ends of the coil were sealed into the ends of small glass tubes within which were stout copper wires, contact being made by mercury. It is necessary that the copper wires be heavy so that they may not become heated, and thus superheat the vapor coming into contact with the glass tubes encasing them.

The temperatures at which distillations took place were read from small standardized Anschütz thermometers, whose mercury threads were entirely within the vapor, so that no correction for projecting mercury thread was necessary. The bulb of the thermometer was placed opposit the entrance to the hood, in order to measure the temperature of the vapor actually admitted—a point especially emphasized by Louguinine, who nevertheless merely inferred the temperature from the barometric pressure and the coefficients expressing the dependence of boiling point on pressure.

Another point, usually neglected, is worthy of brief notice. Before the liquid comes to the boiling point, an appreciable quantity of vapor may pass over and be condensed. Obviously this may introduce error, since the assumption is made, in calculating the result, that all the vapor was at the boiling point of the liquid. Moreover, the heat of vaporization is different at different temperatures. In the present experiments this cause of error was eliminated by providing the vaporizer with an outlet and stopcock above, and by passing a very slow current of dried air backwards through the condenser coil and vaporizer until the liquid was boiling at a lively rate, and the temperature of the whole interior was quite at the boiling point of the liquid. This air prevented the vapor from passing into the condenser, so that no premature condensation was possible; its initial temperature was kept close to that of the calorimeter.

Preliminary experiments were made to find whether or not the proximity of the hot coil of platinum wire might superheat the vapor passing in its downward course to the condenser. The wire was first made into a coil about 3 cm. in diameter, and a thermometer suspended therein, the bulb of the thermometer being at the center. The coil and ther-

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mometer bulb were then immersed in distilled water in a large open test tube, the current was connected, and the temperature noted at which boiling occurred. The coil was then made about 2 cm. in diameter and the process repeated; finally the wire was coiled as tightly as possible around the thermometer bulb, without actual contact, and the temperature at which boiling took place was noted as before. It was found that there was no danger of superheating from this source, as the temperature recorded by the thermometer was exactly the same in all three cases. As long as the wire is covered with liquid, it matters not whether the resistance wire is coiled loosely or closely around the tube through which the vapor is passing. Hence vapor passing through a tube similarly encircled by hot wire must be free from superheating.

The calorimeter, of about 1.5 liters capacity, was made of thin nickel-plated sheet copper, highly burnished on the outside. It was almost filled with water, and is shown in Fig. 5 (D, D). The condenser (A) within the calorimeter was constructed of block tin, the joints being soldered by tin only; it consisted of a spiral tube, 1 meter long and 3 millimeters in internal diameter, coiled in four turns, with a tin cylinder 10 centimeters long and 3 centimeters in diameter at the bottom to serve as a receptacle for the condensed liquid. The tin cylinder had an outlet tube, leading directly up to the air of the room. The tin coil and cylinder together weighed 436.7 grams. The outlet tube or break of the vaporizer was attached to the worm by a short piece of pure rubber tubing (B). Various preliminary experiments were made as to the position of this joint in relation to the water of the calorimeter, but the details need not be given. Finally, the arrangements shown in the figure was adopted; the silvered jacket of the vaporizer was immersed to the depth of about a centimeter under the water. The water-line was thus protected from heat by the vacuum jacket, and abnormal evaporation and cooling at this point were therefore avoided.

The stirrer (C) within the calorimeter was of the propeller pattern, having six blades, each 1 centimeter long. It was made of copper, and, in order to prevent loss of heat by conduction, extended only to the surface of the water, where it joined a shaft of hard rubber to which was attached the driving mechanism. The scarcely perceptible evolution of heat from the stirrer, being directly proportional to the time of the experiment, was included with the warming due to the proximity of the vaporizer in a single time correction, and thus eliminated from the result.

The heat capacity of the solid parts of the calorimeter was equivalent to 53.4 grams of water, the separate parts amounting to the following quantities. The finished copper calorimetric vessel weighed 299.95 grams. It was "plated" inside and out with a thin electrolytic film

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of burnished nickel, which has a specific heat so near that of copper as to cause no appreciable difference in the heat capacity of the whole. The copper vessel was soldered with about 4 grams of solder, the solder consisting half of lead and half of tin, and having therefore a specific heat of about half that of copper. The calorimeter vessel with its nickel

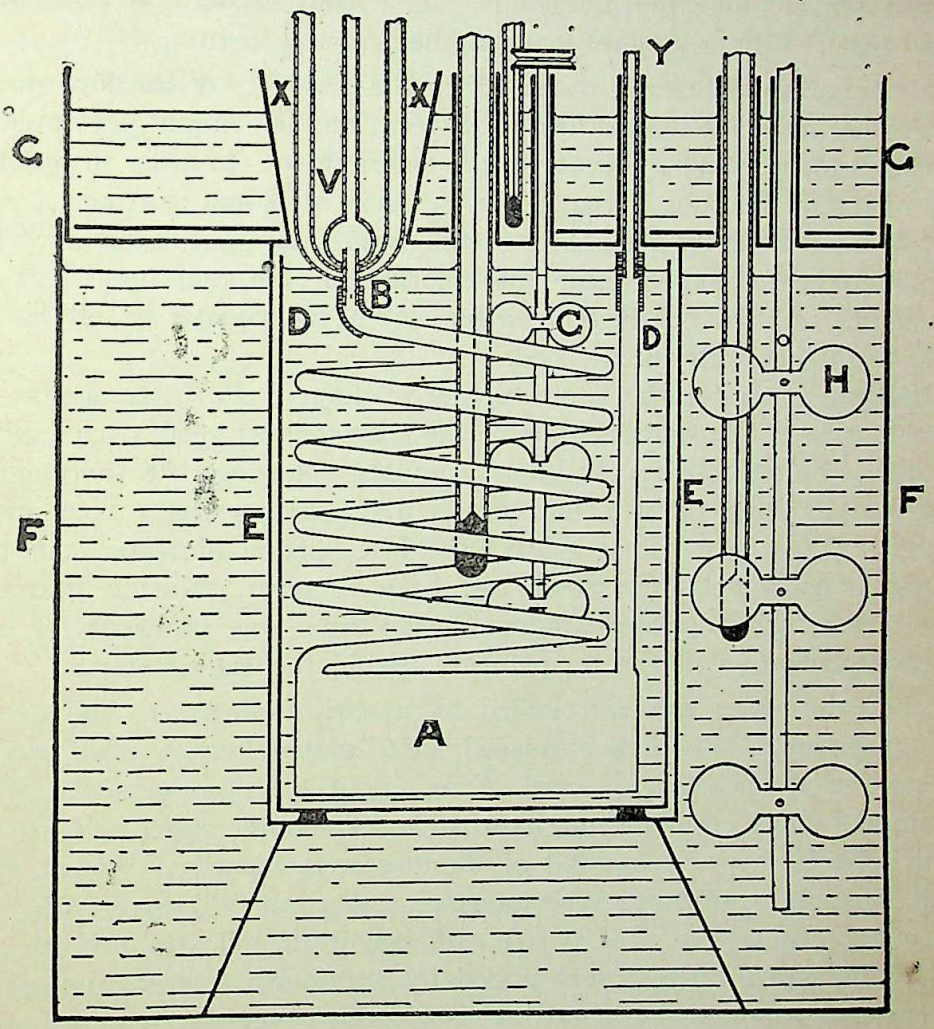


Fig. 5.—The calorimeter. The vaporizer (V) is set within a large hole (XX) in the cover. At B is attached the condenser A immersed in water contained in the calorimeter. Between the jacketing vessels E and F is dilute alkali, into which sulfuric acid is dropped in order that the temperature of the surroundings should keep pace with that of the calorimeter proper. C is a stirrer within the calorimeter, H one in the outside vessel.

and solder was therefore approximately equivalent to the pure copper vessel, weighing 298 grams, and had a heat capacity equivalent to 27.7 grams of water, the specific heat of copper at 21° being about 0.093. It may be noted that the weight of the copper vessel need not be known within two or three grams, for this corresponds to the limit of possible

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accuracy of the thermometric part of the experimentation. The pure tin condenser weighed 436.7 grams, and therefore had a heat capacity equivalent to 23.6 grams of water, the specific heat of tin at 21° being about 0.054.[1] The thermometer was found by the method of Ostwald-Luther[2] to have a heat capacity equivalent to 1.4 grams of water; and the copper stirrer, weighing 7.7 grams, had a heat capacity of 0.7 on the same basis. These weights have as their sum 53.4 grams.

An important matter of detail lay in the discovery of the time needed for equalization of temperature between the hot liquid accumulating in the condenser and the water of the calorimeter. In order to test this, a glass funnel was substituted for the vaporizer at B, and 17 grams of water were poured little by little through this funnel during 5 minutes. There being no heated object near the calorimeter, the radiation effect was negligible, and the rise in temperature of the calorimeter water was due only to the hot water introduced.

Immediately after the addition, the reading of the thermometer was a trifle over 1°; in another minute the thermometer read 1.101°; in yet another minute 1.104°. In the 3 minutes following, the thermometer rose 0.001° each minute, and finally remained perfectly constant at 1.107°. Thus in 5 minutes after the last portion of water had been added a constant temperature had been attained, showing that with the rate of stirring usually adopted, this time was sufficient for complete equalization of the temperature within the calorimeter.

The calorimeter was surrounded by a narrow air space, bounded by a copper can (E) with a burnished nickel-plated lining. This was immersed in a much larger vessel (F) of about ten liters capacity, which contained dilute crude sodium hydroxide. The outer vessel was provided with a basin-shaped cover (G) of about 4 liters capacity, through which were several openings for thermometers, vaporizer (V), stirrer, etc. The bottom of the cover was coated with bright tin foil. In this way the calorimeter was entirely surrounded by a uniform temperature, except where the vaporizer protruded through the cover. A powerful stirrer (H), revolving at the rate of 250 revolutions per minute and driven by an electric motor, kept the lower alkaline solution in violent agitation while the solution in the cover was more gently agitated by means of a perforated ring of heavy sheet copper, lifted by an electric motor and allowed to fall by its own weight. The stirring in the cover need not be so energetic as that below, since the temperature in this part of the bath need not be so accurately adjusted as in the lower compartment.

[1] The specific heats of copper and tin usually given (0.094 and 0.055 respectively) correspond to the range between 20° and 100°. The values given above take account of the decrease with decreasing temperature.

[2] Ostwald-Luther, Handbuch, p. 300 (1910).

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As the temperature in the calorimeter rose, because of the condensation of the vaporized liquid, concentrated sulfuric acid was run from burets into both jacketing compartments, so that the environment around the calorimeter was changed in temperature as fast as the calorimeter itself. The details are so similar to those of the other applications of this adiabatic method that they need not be reviewed. The stirring was so effective that the thermometers in different parts of the bath all rose at practically the same rate.

It was found possible to follow the rising temperature of the calorimeter within 0.05° in the lower compartment and within 0.1° in the upper compartment throughout the entire course of the experiment. Suitable tests proved that with so small a difference in temperature there was no danger of appreciable heat exchange with the surroundings during the brief progress of a determination.

The rise in temperature of the calorimeter was measured by a carefully standardized Beckmann thermometer, having a slender bulb and rather a long scale. Readings to 0.001° were made with certainty by means of a lens. The standardization was effected with very great care by comparison with two Baudin thermometers standardized by the Bureau des Poids et Mesures of Paris. The comparison was conducted by immersing all the thermometers in the water of the adiabatic calorimeter surrounded by its jacket. The calorimeter was covered tightly with a non-conducting cover through which the thermometers and stirrer passed, and the thermometer to be studied was immersed to the depth at which it was subsequently to be used. All the thermometers were placed as closely together as possible in order to insure their having the same temperature. The temperature of the calorimeter water could be held perfectly constant for any desired length of time, so that there was no error due to the lag in any of the thermometers. Readings were made (after gently tapping the thermometers) at every $^1/_{10}$° mark, and the corrections were calculated with due account of the correction for the various standardized thermometers used. The Baudin thermometers had previously been found to agree very closely with an accurate Fuess thermometer, which in its turn had been carefully studied by the Reichsanstalt of Berlin.

The various parts of the apparatus having been described in detail, the actual execution of the experimental work may now be considered.

As may have been inferred, many preliminary determinations were made in order to determin the best conditions, and the various dangers to be avoided: Water, having been the liquid most studied by others, was chosen as the most desirable substance with which to test the apparatus and method.

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Over thirty trials were made with the object of finding the best position of the vaporizer and testing various devices to prevent radiation.

Finally the following method of experimentation was adopted: The pan-like copper cover (G, Fig. 5) of the calorimeter jacket was placed temporarily upon a raised stand which permitted easy access to its lower surface; the vaporizer (V) containing the liquid to be investigated was adjusted into its place (packing the space X between its silvered envelope and the copper cover with cotton wool) the empty weighed condenser (A) was then attached to the beak of the vaporizer (B) as it protruded beneath the elevated copper cover, and the thermometer and stirrer were arranged in their orifices. Meanwhile the calorimeter had been almost filled with a weighed amount of water as about 20°, and the jacketing crude alkaline solutions had been adjusted at exactly the same temperature. When all was ready, the copper cover with the suspended condenser was placed in position over the calorimeter, the condenser being immersed very carefully in the calorimeter water. The silvered beak of the vaporizer itself dipped about a centimeter under the surface, as shown in the diagram. The slow backward current of air, which served to prevent the access of vapor to the condenser until all was ready, was then driven through the apparatus, and at the same time the heating electrical current was turned on within the vaporizer. When the liquid was actively boiling, a careful study of the radiation-conduction effect on the calorimeter was made. This having been accomplished, the actual experiment could begin; the stopcock (K, Fig. 4) above was closed and the backward current of air discontinued. The rapid current of vapor was thus suddenly switched into the condenser, and the temperature of the calorimeter began to rise at a rapid rate. This rate was continuously matched in the environing alkali by admitting acid in suitable quantities, and the experiment proceeded very smoothly until a rise of about 4 degrees had been accomplished. Finally the stopcock (K, Fig. 4) above the vaporizer was suddenly opened, the posterior outlet (Y, Fig. 5) of the condenser closed, and the electric current cut off. The vapor forming was then free to escape into the air, and when boiling stopped the condensed liquid was not drawn back into the vaporizer by the sudden vacuum formed upon cessation of boiling. For at least five minutes afterwards, the temperature of the calorimeter was read every minute with as great care as at first. After dismounting the apparatus the condensing coil was dried outside and weighed, and the experiment was thus brought to a close.

The increasing temperature and the increasing heat capacity of the calorimetric system during an experiment cause complications in the calculation which have usually received insufficient attention. At the beginning, the heat capacity of the calorimeter is that of the solid

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apparatus and the water in which the coil is immersed. As the experiment proceeds, this heat capacity is augmented by the liquid which collects within the condenser. At the end of the distillation the heat capacity of the calorimetric system reaches its maximum. Evidently the value used in the calculation must be taken as the initial heat capacity plus the heat capacity of half the condensed liquid.

Heat is radiated and conducted from the hot vaporizer into the calorimetric system, and correction of this unavoidable complication must be applied. The correction is primarily based upon the measurement of the heat gained during the preliminary minutes before the experiment has been begun, in the usual fashion; but it must be remembered that this value does not apply exactly to the end of the experiment, because the calorimeter has then risen in temperature, and therefore cannot take so much heat from the vaporizer as before. For example, if the temperature of the calorimeter is 20° at first and 24° at the conclusion of the experiment, and if the vaporizer has a temperature of 100°, it is evident that the difference of temperature between the vaporizer and the calorimeter is 80° at first and only 76° at the end. Hence, if the calorimeter gains 0.009° during each preliminary minute, it will be expected to gain only $76/80 \times 0.009° = 0.0085$ during each final minute, and intermediate values during the intervening period. The method of correction for this changing effect is obvious and was easily applied. This practice was justified by the actual results, for the warming effects of the hot vaporizer was always found to be less after the experiment than before. The diminution was manifest even before the vaporizer itself had cooled considerably.

The changing condition of the calorimeter involved a similar detail in the calculation of the heat given out by cooling the condensed liquid from its boiling point to the temperature of the condenser. The heat actually measured in the calorimeter was due, of course, not only to the heat given out by condensation, but also to that given out by the condensed liquid in falling from the temperature of the vaporizer to that of the calorimeter. The first portion of condensed liquid is cooled to the initial temperature of the calorimeter, the last portion only to the somewhat higher final temperature. Obviously here again the mean temperature must be taken in the calculation. Thus, if the experiment began at 20° and ended at 24° and the barometer indicated 760 mm., the first drop of water was cooled through 80°, the last through only 76°. Obviously here again the average value, 78°, should be taken in the calculation. It is easy to show by means of the calculus that all these compromises in the calculation are legitimate.

The amount of water evaporating into the small air-space around the

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calorimeter during an experiment was negligible both in weight and in thermal effect.

There follow, as a typical example, the complete data and computation of a single case, the second given in the table, selected at random from results.

For five minutes preceding the experiment, the calorimeter gained at a perfectly constant rate of 0.009° per minute. When this was certain the vapor was turned into the condensing coil, and after five minutes more the electric current of 14 amperes was stopped, and the vapor prevented from gaining further access to the coil. In yet five minutes the calorimeter had settled down once more to a rate of increase in temperature corresponding to that observed at first, that is to say, 0.0085° per minute, clearly due only to radiation and condensation from the vaporizer. The heat from the actual condensation had all been imparted to the calorimeter, hence the experiment was considered as concluded. The several data and the simple calculation depending upon them are given below. The barometric pressure was exactly 760.0, hence the steam entered the condenser at 100.0°.

In calculating the heat given out in cooling a gram of water from 100° to the mean temperature of the calorimeter (21.42°) the figures of Barnes[1]

HEAT OF VAPORIZATION OF WATER.

Determination No. 2.

Time when reading was taken.	Observed thermom. reading in water in calorimeter (uncorrected).	Increase in temperature per minute.
1.21	0.090°	...
1.22	0.098	0.008
1.23	0.107	0.009
1.24	0.116	0.009
1.25	0.125	0.009
1.26	0.134	0.009
1.27	0.143	0.009
1.28	0.152	0.009
1.29	0.161	0.009
1.29 Vapor turned into coil.		Average, 0.009
1.34 Electric current stopped.		
1.35	5.100	...
1.36	5.117	0.017
1.37	5.128	0.009
1.38	5.138	0.010
1.39	5.147[2]	0.009
1.40	5.155	0.008
1.41	5.164	0.009

[1] Landolt and Börnstein, Tabellen, pp. 393 and 810 (Berlin, 1905).

[2] Point at which rise of temperature due to condensation of vapor ceased. Further increase of temperature, since the rise did not exceed 0.0085° per minute, was due to radiation from vaporizer.

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	Reading of thermometer.	Correction to reduce reading to true temperature.	Corrected temperature hydrogen scale.
Final temperature	5.147°	+18.787	23.934°
Initial temperature	0.161°	+18.760	18.921°
Total rise in temperature			=5.013°
Rise due to radiation and conduction (2.5 × 0.009° + 7.5 × 0.0085)			=0.086°
Rise in temperature due solely to condensation of vapor and cooling of resulting liquid to temperature of calorimeter			=4.927°
Water equivalent of calorimeter and fittings			53.4 g.
Water equivalent of water in calorimeter			1252.9
Water equivalent of ½ the liquid condensed			5.26
Total water equivalent			1311.56 g.
Weight of condensing coil and condensed liquid			447.219
Weight of condensing coil alone			436.705
Weight of vapor condensed (liquid vaporized)			10.514 g.

Total heat effect per gram $= \frac{1311.6 \times 4.927}{10.514} = 614.63$ cals. at 21°.

Heat given out by cooling 1 gram from 100.0°—21.42°= 78.67 cals. at 21°.

Uncorrected heat of vaporization of *one gram* of water = 536.0 cals. at 21°.

were employed, because they probably represent most nearly the present standard of temperature. By graphic integration, the average specific heat of water over this range was found to be 1.0012 times the value at 21.4°; hence is calculated the value 78.67 calories above, corresponding to a fall of 78.58°. The 21° calorie is apparently about 0.9985 times the 15° calorie, hence in terms of the latter the result would be 535.2.

Six determinations were conducted in this way with this vaporizer, two of them being run very slowly and the other with increasing speed. For the slowest about 11 or 12 amperes were usually necessary, and 17 or 18 amperes were required for the fastest. The results are rearranged in the table and renumbered in order of speed, beginning with the fastest, so as to make the dependence of the results upon the speed more clearly manifest. The first five experiments made early in December, 1907, were all consecutive; but that numbered 6 was executed long after the others (in January, 1908), after the vacuum jacket had been used for higher-boiling liquids, and had unfortunately cracked. Except for its somewhat larger warming correction, no essential difference could be detected between its results and that of the preceding experiment, carried out at the same rate. The last experiment was conducted under a pressure of 757 millimeters of mercury, the others were at normal pressure of 760 millimeters.

The table explains itself.

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HEAT OF EVAPORATION OF WATER.

Series I, with Vaporizer I.

No. of experiment.	Observed weight condensed water (in air).	Time in minutes.	Time for one gram.	Rise of temperature corrected for radiation from vaporizer	Water equivalent total.	Difference between temperature of vaporization and mean temperature.	Heat of vaporization + heat of cooling to temperature of calorimeter.	Heat of vaporization of 1 gram (uncorrected) in 21° calories.
1	8.319	3.0	0.36	3.921	1307.6	78.9	616.3	537.4
2	10.514	5.0	0.48	4.927	1311.6	78.6	614.6	536.0
3	8.283	4.25	0.51	3.895	1307.8	78.8	614.9	536.1
4	9.558	8.5	0.89	4.473	1309.3	78.6	612.6	534.0
5	8.368	9.0	1.07	3.896	1310.2	78.3	609.9	531.6
6	8.398	9.0	1.07	3.916	1309.4	78.4	610.5	532.1

It will be noticed that the figure in the last column falls from 537.4 calories per gram, the result of the fastest determination, to 531.8 calories, in the two slowest—a change of about 1 per cent.

This definit march of the results seems to be referable only to the loss of heat by premature condensation in the part of the tube between the trap and the condenser—a defect in the method which is inevitable, for the vaporizer could hardly be brought closer to the calorimeter than it was in these experiments.

When the results are plotted, the values for the heat of vaporization being laid out in the direction of ordinates, and the time required for vaporization of 1 gram laid out in the direction of abscissas, the linear

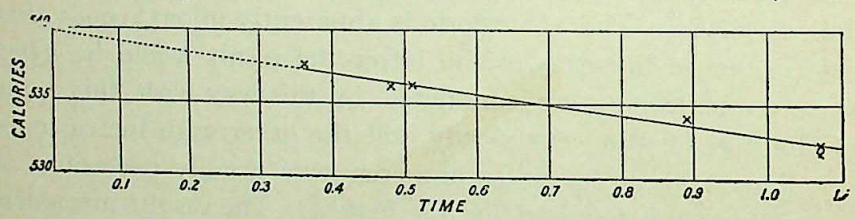


Fig. 6.—The heat of evaporation of water; first series. Time in fractions of a minute is plotted in the direction of abscissas, and heat of evaporation (in 21° calories) in the direction of ordinates. The dotted line is an extrapolation, giving the value for a hypothetical instantaneous experiment.

tendency of the results is manifest. The greatest departure of any single result from the straight line representing their average tendency is only 0.6 calorie, or 0.1 per cent. of the total thermal quantity being measured. This corresponds to an error of thermometric reading of 0.004°. The agreement therefore is as close as could be expected.

By extrapolation to zero time the value 539.6 (cal. 21°) is obtained for the heat of vaporization of a gram of water weighed in air—a value from which the effect of premature condensation must have been elim-

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inated, because there is every reason to believe that this disturbing phenomenon is directly dependent upon the time consumed in the experiment, and that if the experiment could be performed instantaneously the error would wholly disappear. This value becomes 538.8 in terms of the calorie at 15°.

Inspection of the curve shows that the loss of heat in 1 minute must have been 7.0 small calories from this apparatus under these circumstances, and each of the results is evidently to be reduced to a common basis by adding to it this value multiplied by the fraction of a minute required for the vaporization of 1 gram. The results, then, become respectively 539.9, 539.4, 539.7, 540.2, 539.1 and 539.6, in the mean 539.6 (cal. 21°), essentially the same as the value found by the graphic extrapolation, upon which indeed the values are directly dependent.

Feeling that it was desirable to test these conclusions in another apparatus, a new vaporizer was made—unfortunately, however, with a somewhat wider and heavier exit tube. In this apparatus both the warming effect of the vaporizer upon the calorimeter and the loss of heat from premature condensation were greater than before—the former

HEAT OF EVAPORATION OF WATER.

Series II, with Vaporizer II.

No. of experiment.	Observed weight condensed water (in air).	Time in minutes.	Time for one gram.	Rise of temperature corrected for radiation from vaporizer.	Water equivalent total.	Difference between temperature of vaporization and mean temperature.	Heat of vaporization + heat of cooling to temperature of calorimeter.	Heat of vaporization of 1 gram (uncorrected) in 21° calories.
7	7.435	3.0	0.40	3.484	1309.0	78.62	613.5	534.9
8	7.170	3.0	0.42	3.376	1306.9	78.95	615.4	536.4
9	8.740	4.5	0.52	4.091	1308.6	78.54	612.5	534.0
10	8.625	5.0	0.58	4.034	1308.6	78.59	612.1	533.5
11	9.040	10.0	1.11	4.190	1310.1	78.69	607.3	528.6
12	9.150	10.0	1.09	4.250	1307.8	78.54	607.5	529.0

instead of being about 0.009° per minute became about 0.013, and the correction for premature condensation also increasing from 7 calories per minute to nearly 9.7 calories per minute. The determinations were also somewhat less concordant than before, as was to have been expected on account of the larger correction for radiation and conduction. Nevertheless they add valuable confirmatory evidence to the results given in the previous series, and accordingly are recorded in the following table arranged in the same way as those. Experiments 7, 8, 9, 10 and 11 were consecutive, and were made on the 7th and 8th of April, 1908. Experiment 12 was made at another time, but accords satisfactorily with 11, having about the same rate. During Nos. 7, 9 and 10 the barom-

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eter stood at 763 millimeters, during Nos. 8 and 11 at 766 millimeters, and during No. 12 at 762 millimeters.

On extrapolating the steeper but fairly consistent straight line drawn through these determinations, the value 539.3 (cal. 21°) is obtained for the heat of vaporization of a gram of water, a value only about 0.06 per cent. lower than that found in the previous series. A part of this difference is due to the slightly higher temperature of boiling in the second series, caused by the greater pressure.

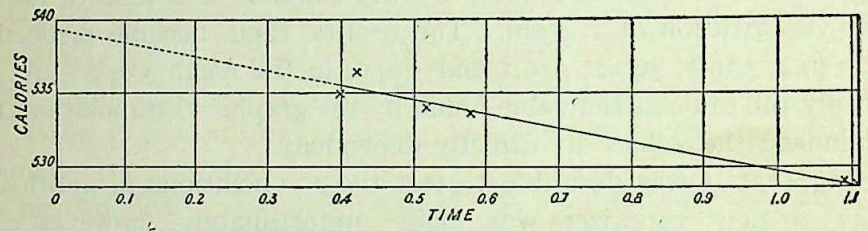


Fig. 7.—The heat of evaporation of water; second series. Time in fractions of a minute is plotted in the direction of abscissas, and heat of evaporation (in 21° calories) in the direction of ordinates. The dotted line is an extrapolation, giving the value for a hypothetical instantaneous experiment.

The individual determinations may be corrected by adding to them 9.65 multiplied by the time needed for vaporization of 1 gram, because the loss of heat is found through extrapolation to have been 9.65 small calories per minute. Corrected in this way the five determinations become respectively 538.8, 540.5, 539.0, 539.1, 539.3, on the average 539.3 as given before. The average of the results given in this series and those given in the previous series is 539.45. As the second decimal place has no significance, this may be rounded off to 539.5, giving the first series preference, partly because the pressure was more nearly normal, and partly because the apparatus was undoubtedly better and the series more concordant. This value becomes 538.7 in terms of the calorie at 15°. If the weight of the water is reduced to the vacuum standard, both of these figures are diminished by 0.11 per cent. The resulting values may be given in a brief table, together with the same quantity expressed in terms of the c. g. s. units:

FINAL RESULT.

Latent heat of evaporation at 100° of 1.0000 gram (in vacuum) of water equals:

538.9 $cal._{21°}$ or 0.5389 $cal._{21°}$
538.1 $cal._{15°}$ or 0.5381 $cal._{15°}$
2251 joules or 2.251 kilojoules

In all the subsequent work the first vaporizer was used, even although its vacuum had been destroyed; and it continued to give excellent results with other substances. The communication of these results must be left for a future publication, partly because the necessary specific heats

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of the liquids are not yet well enough known. One point, however, in connection with the results may advantageously be mentioned here, because it strengthens highly one's faith in the method of extrapolation employed to eliminate the effect of premature condensation. The loss of heat per gram was 7 calories per minute with steam in the best apparatus (Vaporizer I). With liquids of lower boiling point the loss should be less; with liquids of higher boiling point the loss should be more, if the inference is really justified. As a matter of fact precisely this phenomenon was noticed with different liquids. For example in the case of benzene, where the difference between the temperature of the vaporizer and that of the calorimeter amounted to 60° instead of to about 80°, the loss per minute amounted to about 5.2 calories per minute,[1] a figure strictly proportional to the number 7.0 found in the case of water. Again with ethyl butyrate, boiling at 122°, the difference between the temperature of the vaporizer and that of the calorimeter was 102° instead of 80°, a fall of temperature which should correspond to a loss of heat of about 9 calories per minute, and the actual loss was found to be about 9.2 calories per minute, an amount as close as could be expected to the computed result. Moreover, in the case of methyl formate, boiling at 32°, the time of the experiment made practically no difference at all in the observed value for the heat of vaporization. Thus t seems perfectly clear that the march in the results is really due to an illicit loss of heat, and that the method employed for correcting the results is the best that can be devized. In conclusion the remark may be made that unfortunate as this inevitable difficulty with the method is, it is no more unfortunate than similar difficulties which come into any other method for determining the latent heat of vaporization. As has been more than once pointed out, the very nature of the problem renders impossible a method wholly free from some sort of correction. Even Henning's far more complicated method had its own difficulties of a somewhat similar kind, as a perusal of his paper will show.

The comparison of our value for the heat of vaporization of a gram of water weighed in vacuum, 538.9 $cal._{21°}$ (or 538.1 $cal._{15°}$), with the work of others, speaks strongly in its favor. The value given by Regnault, 536.7, is unquestionably too low. Henning's value 538.25 $cal._{15°}$ was found at 100.6°. Corrected to 100°, this would be 538.7 $cal._{15°}$, a value only a trifle above ours. Joly,[2] Harker[3] and Smith,[3] likewise obtained values near 540.

[1] This figure applies only to Vaporizer I, not to the preliminary form used in the benzene series given on p. 13. In the early form the loss per minute was over 9 calories with benzene.

[2] *Phil. Trans.*, 186, 328 (1895). Dependent on Joly's value for the mean calorie between 12° and 100°.

[3] *Loc. cit.*

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In conclusion we are glad to express our gratitude to the Carnegie Institution of Washington, for generous pecuniary assistance.

Summary.

1. The method of Berthelot and Kahlenberg for determining heats of vaporization has been modified in such a way as to diminish greatly the errors inherent in the experimentation. A Dewar vessel was used as a vaporizer and the calorimetric work was strictly adiabatic.

2. A serious persistent disturbing effect, amounting to about 0.1 per cent. of the total per minute, was eliminated by conducting experiments at different speeds and extrapolating the results to a hypothetical instantaneous experiment from which the disturbing effect may be supposed to be eliminated, because this was found to depend essentially upon time. The disturbing effect was probably premature condensation in the very narrow zone between the vaporizer and the condenser.

3. The heat of vaporization of a true gram of water was found by this method to be 538.9 $cal._{21}°$ or 2.251 kilojoules per gram. A gram molecule therefore requires 9.707 $cal._{21}°$ or 40.54 kilojoules, when the vaporization is conducted at 100° (O = 16.000, 1 $cal._{21}°$ = 4.177 kilojoules).

4. Comparison of this figure with the results of others shows that the method is trustworthy and suitable for general use.

5. Numerous other liquids also have been used in the apparatus, and consistent results with them have been obtained. These will be communicated in a future paper, when the specific heats of the liquids have been determined.

CAMBRIDGE, MASS.

THE POSSIBLE SOLID SOLUTION OF WATER IN CRYSTALS.

BY THEODORE W. RICHARDS.

Received April 25, 1911.

In a recent paper Perdue and Hulett[1] have published the results of several careful analyses of cadmium sulfate, which deserve an adequate explanation. According to these determinations the amount of cadmium both in the hydrated sulfate and in the anhydrous sulfate is less than that required by the usually accepted atomic weight of cadmium, sulfur, oxygen and hydrogen, and the formulas $3CdSO_4.8H_2O$ and $CdSO_4$ respectively.

The determination of the cadmium seems to have been well executed; the experimenters adopted two well known and long tested methods, namely, the use of mercury as a receptacle for the electrolytic precipitate

[1] Perdue and Hulett, *J. Physic. Chem.*, 15, 147 (1911).

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on the one hand[1] and the method of washing the deposit while it is still a cathode[2] on the other hand.

Perdue and Hulett evidently believe that their results are best explained by assuming an error in the accepted atomic weight of cadmium, but this atomic weight rests on the very careful work of Baxter[3] carried out by methods quite as well tested and trustworthy as those used by Hulett; and while no work of this sort even in the very most experienced hands can be considered as quite wholly final, the presumption is decidedly in favor of the accuracy of the generally accepted value for cadmium.

Here is a definit contradiction. An explanation of the inconsistency is important, not only to those interested in the atomic weights, but also to physical chemists, especially those concerned with the causes which lie back of the difficulties of analytical chemistry. I shall endeavor to show that in all probability both sets of data are correct, and that the difficulty lies solely in the interpretation.

If the fact discovered by the Princeton investigators stood alone, an attempt at explanation might be hazardous; but their results are wholly in line with many other observations made in recent years concerning the amount of water in crystallized salts. Over two decades ago it was shown in the Chemical Laboratory of Harvard College that crystallized copper sulfate also contains an excessive amount of water, about 36.11 per cent., instead of the theoretical quantity 36.07.[4] Moreover, the salt still retained after drying to constant weight at 400° about 0.12 per cent. of this quantity, as nearly as could be estimated at that time. This water only escaped when the salt itself was decomposed. Finely powdering the salt and using very clear crystals did not seem to diminish very greatly the excess of water. Many other similar cases might be cited.

In a more recent paper, read at the meeting of the American Philosophical Society in 1903,[5] I took occasion to point out that included solvent is a great source of error in dealing with crystals obtained from solutions, quoting many well-recognized cases, such as for example the inclusion of solvent in crystallized silver, first noticed by Lord Rayleigh, later verified in the Chemical Laboratory of Harvard College, and recently confirmed by Hulett himself. It was made clear that this cause of error must be taken into account whenever a crystallized salt is weighed. Yet

[1] W. Gibbs, *Am. Chem. J.*, 13, 571; Luckow, *Z. anal. Chem.*, 26, 113; Vortmann, *Ber.*, 24, 2749; E. F. Smith, "Electro-analysis," p. 58. This method Perdue and Hulett improved by using an amalgamated platinum receptacle.

[2] See for example, Classen, *Ausgewählte Methoden der analytischen Chemie*, 1, 112 (1901).

[3] Baxter, *Pub. Car. Inst.*, 135, 3–26 (1910).

[4] Richards, *Proc. Am. Acad.*, 26, 267 (1891); also, *Z. anorg. Chem.*, 1, 179 (1892).

[5] Richards, "The Inclusion and Occlusion of Solvent in Crystals," *Proc. Am. Phil. Soc.*, 42, 28 (1903); *Z. physik. Chem.*, 46, 189 (1903).

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another point was emphasized in this paper, namely, the frequent presence of adsorbed moisture in the surface of crystals. This increases, of course, as the surface is increased; therefore the act of powdering, in order to break up the cells containing mother liquor, increases the adsorption.

Nevertheless for the recent work of Hulett and the old work on copper sulfate neither of these explanations seems to be wholly sufficient, although probably explaining a part of the discrepancy as regards the crystallized salt. The crystals employed in both cases were clear and transparent, and (at any rate in the case of copper sulfate) probably enough crushing was effected to open most of the objectionable cells. If any considerable amount of enclosed mother liquor had been present in enclosed cells, the crystals would have been expected to appear slightly cloudy in places; but as far as appearances went they were homogeneous. One is inclined therefore to search for a superposed effect which might account for this apparent homogeneity.

At the close of the previously mentioned paper on inclusion and occlusion of solvent in crystals[1] a hint is given of a possible explanation for the existence of a surplus of water in crystals; and because, as time goes on, this explanation seems more and more probable to me, I venture to amplify it now.

May it not be that crystals formed from aqueous solution have power to *dissolve* water in the form of a solid solution? In his interesting and conclusive paper on solid solutions van't Hoff[2] showed that solid substances may dissolve not only isomorphous substances, but also in greater or less amounts almost any sort of material; and he pointed to the colors of gems and to a great variety of other well known phenomena as examples.[3] He did not suggest that a solvent also might thus be dissolved by the crystal in the act of crystal formation from a solution; but why should the solvent, so available for this purpose, be overlooked by the crystal? Indeed, the conditions of the formation of a crystal from an aqueous solution suggest that every such crystal should be a saturated solid solution of water in the crystallized salt; and the extent to which the water would thus be dissolved by the crystals must, of course, depend upon the specific nature of the substances concerned.

This hypothesis that crystals contain not only included and adsorbed but also *dissolved* water in the form of solid solution receives striking support from a recent paper by D. Gernez, "The Nature of the Change in Crystals of Sodium Sulfate Heptahydrate in Contact with Crystals of the Decahydrate."[4] Gernez points out that metastable crystals such

[1] Richards, *Loc. cit.*

[2] van't Hoff, *Z. physik. Chem.*, 5, 322 (1890).

[3] Attention may be called to the adsorption of coal-tar colors by crystals, Marc, *Z. physik. Chem.*, 75, 710 (1911).

[4] Gernez, *C. r.*, 149, 77–84 (1909).

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as the heptahydrate of sodium sulfate, while forming traces of the higher hydrate (in this case the decahydrate) within themselves, on being inoculated with another crystal of this substance, show no evidence of the formation at the same time of the hydrate poorer in water.

Gernez supposed that the extra water necessary to form this decahydrate came from included water contained in imprisoning cells, but this seems to me to supply only a partial explanation. The appearance of such a changed crystal suggests a more intimate distribution of the change than would be possible according to this suggestion. On the other hand, if water were dissolved in the form of solid solution, the result would be expected to be just that which is actually observed. The dissolved water together with some of the heptahydrate might form crystals of the decahydrate throughout the mass, enough to render it opaque, but leaving the remainder of the heptahydrate unchanged.

The recent revival of the discussion concerning the loss of superfluous water (not water of crystallization) occasioned by powdering crystals has offered no valid argument in disagreement with the idea that water may be dissolved in solid solution by the crystals. The work of Baker and Adlam[1] confirms the existence of superfluous water in crystals and confirms also the fact noticed by the author twenty years ago that this water is partially but not wholly lost upon powdering. This could have happened from a solid solution almost as easily as from included cells of mother liquor. The amount of water dissolved by a crystal at the moment of formation must be a function of the aqueous vapor pressure of the mother liquor at that moment. Such a crystal could lose water from its surface, into an atmosphere which contained less aqueous vapor pressure. The greater the surface the more chance there would be for the loss of water, because water cannot escape from the interior of the crystals.

All these considerations taken together present a striking argument for the asssumption of the solid solution of water in crystals; and the hypothesis seems to have very little against it. The existence of too much water and therefore too little cadmium and copper in their respective crystallized sulfates becomes from this point of view an entirely reasonable phenomenon. The lack of numerical consistency is then to be traced to the nature of the crystallized salt rather than to an error in any of the accepted atomic weights, or in the analytical results of either Baxter or Perdue and Hulett.

If this is the case, probably different amounts of water are dissolved by crystals at different temperatures. Thus $3CdSO_4.8H_2O$ would probably dissolve different amounts of water at 70° and at 0°. The presence of

[1] H. B. Baker and G. H. J. Adlam, *J. Chem. Soc.*, 99, 507 (1911). See also Richards, *Z. anorg. Chem.*, 1, 79 (1892); Richards, *Z. physik. Chem.*, 46, 189 (1903).

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alcohol or other miscible liquid together with the water would diminish the water dissolved by the crystals at the moment of their formation. This difference in aqueous content would probably affect slightly all the properties of the crystals. Moreover, in all probability water is dissolved by salts without water of crystallization, as well as by hydrated salts.

All these points are interesting, and will be studied in the near future at Harvard University.

Baker and Adlam in the paper already mentioned describe experiments wherein dried salts were allowed to regain their water of crystallization in a somewhat moist atmosphere, and were found actually to absorb almost exactly the theoretical amount. Under these conditions the hydrated salt would be formed in the presence of an atmosphere less nearly saturated with aqueous vapor than if it were formed from a solution. Therefore the absence of dissolved water is exactly what would be expected. There is, of course, always some doubt in such cases as to whether every innermost pore has been reached by the aqueous vapor. Possibly the agreement with the theoretical was due to the balancing of a slight deficiency of water in the innermost pores with a slight excess adsorbed on the surface. It is evident, however, that these observations cannot be used as an argument against the assumption of the existence of water in solid solution within the crystals formed from an aqueous mother liquor.

One of the phenomena noticed by the author long ago, and more recently by Perdue and Hulett, thus seems to be easily explicable. It remains only to discuss the other, namely, the deficiency of metal in a dried sulfate, due to traces of water held by the salt.

The retention of small amounts of water or other volatil substances by the solid cadmium and copper sulfate at high temperatures may also be examples of solid solution, or these phenomena may be caused merely by the mechanical imprisonment of some traces of the substance by the solid. Many cases of the latter sort are known.[1] Taken together, these two possible sources of error form quite explanation enough to account for the inadequate cadmium content of metal in Perdue and Hulett's ignited sulfate; and of course the per cent. of water found from the loss on ignition would be a variable quantity without much significance, depending upon the relative amounts of the residual water in the dried salt and the crystals.

These considerations reinforce the conclusion italicized in the paper already referred to on the inclusion and occlusion of solvent in crystals, namely, "*it seems to be impossible to determine with the exactness demanded in the most accurate work the true weight of any salt containing water of crystallization.*" The reason for this is because all solids, in the condition

[1] See for example Richards, "On the Occlusion of Gases by Copper Oxide," *Proc. Am. Acad.*, 26, 28 (1891); 28, 200 (1873).

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in which they have been separated from media containing other substances, very likely contain "included" and "occluded" or dissolved impurities.

As has been repeatedly emphasized in papers concerning atomic weight from this laboratory, a solid should be first prepared in such a way as to include or occlude only volatil impurities, and subsequently fused (thus forcing the escape of these volatil impurities), in order to attain purity worthy of serious quantitative consideration in exact work.

Summary.

In this brief paper t has been pointed out that not only inclusion but also *solid solution* of solvent in crystals is to be feared in precise quantitative work. Such solid solution could neither be easily detected nor easily eliminated. The conclusion is reiterated that the solids obtained from an environment containing other substances, such as a solution, are not safely available for exact quantitative work without further treatment. It is pointed out that these considerations afford an adequate explanation for the anomalous results concerning cadmium sulfate obtained by Perdue and Hulett. Therefore no reason for suspecting an error in the accepted atomic weight of cadmium seems to be indicated by these results.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE REFRACTIVE INDEX OF WATER.

BY GREGORY PAUL BAXTER, LAURIE LORNE BURGESS AND HERBERT WILKENS DAUDT.

Received April 13, 1911.

Investigations in this laboratory upon the refractive indices of salt solutions and the refractive constants of dissolved salts,[1] have made desirable an exact knowledge of the index of refraction of water at 25°, a temperature for which this constant has never been accurately found, although many determinations have been made at temperatures somewhat above and below this point. In the following investigation determinations were made not only at 25° but also, for purposes of comparison, at one higher and at one lower temperature.

The accuracy of a determination of the index of refraction of any liquid depends not only upon the sensitiveness and accuracy of the measuring instrument, but also very largely upon the purity of the liquid and the careful regulation of its temperature. It is in the last two respects that many previous investigations have been faulty. In this research these two points received special attention.

The Spectrometer.—The spectrometer was of the Meyerstein type, manufactured by Max Wolz. Its divided circle was graduated in ten-

[1] See following paper.

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minute divisions, and was provided with two verniers on opposit sides of the circle reading directly to ten seconds. It was possible without difficulty, however, to estimate differences of only five seconds. The divided circle could be rotated about the prism support, but could be clamped to the prism support in any desired position. Thus errors in the graduation of the scale could be, at least in large part, avoided by averaging results obtained from different portions of the scale. As a matter of fact no differences of this sort of over five seconds were ever discovered. Both telescope and divided circle were provided with micrometer screws for fine adjustment. The prism could be leveled upon the prism table by means of leveling screws. The slit had parallel edges ground perfectly smooth. The telescope was provided with a cross hair which could be illuminated by means of a Gaus ocular.

The Prism.—The prism was of solid brass, with a cylindrical opening of 3 cm. diameter, 1 cm. less than the diameter of the object lenses of telescope and collimator. For the final experiments this prism was heavily silver-plated. Thick plates of glass were cemented upon the prism by means of Canada balsam. These plates of glass had absolutely plane parallel sides as was shown by viewing in the telescope the reflected image of the slit, when illuminated with monochromatic light, and by interposing the prism between telescope and collimator when the latter were in parallel positions. In the first case no multiple images were produced and in the second the image of the slit was not displaced.

The Adjustment of Temperature.—Since the index of refraction of water for sodium light varies about one unit in the fourth place of decimals per degree, in order to attain an accuracy of one unit in the fifth place of decimals, which was somewhat beyond the accuracy of the spectrometer itself, the temperature must be regulated to one-tenth of a degree Even in a constant temperature room the prism could hardly be expected to remain constant in temperature within so small an amount, owing to heated air currents from the body of the observer and from the lights. Since time is necessary for the accurate setting and reading of the instrument, any method for the simultaneous reading of temperature and setting of the instrument is likely to yield erroneous results, aside from the fact that if the prism contents are changing in temperature, they are likely not to be of uniform density. Hence a device for maintaining the prism and contents at constant temperature was obviously necessary.

For this purpose an air bath was used very similar to those employed by Ruhlmann[1] and later by Perkin.[2] This bath was constructed of two perpendicular concentric cylinders of sheet copper, the smaller 14 cm. in diameter, the larger 21 cm. The space between the cylinders was

[1] *Pogg. Ann.*, 132, 186 (1867).
[2] *J. Chem. Soc.*, 61, 292 (1892).

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divided into three compartments by horizontal copper rings. These compartments were filled with shredded asbestos to ensure better insulation. Openings were cut at suitable places for the introduction of the collimator and telescope, which projected through the walls of the air bath into the interior. The telescope opening was long enough to permit the telescope to swing through an angle of 30°. Both openings were further provided with sliding doors, fitting tightly around the telescope and collimator tubes, by means of which the openings in the air bath could be covered.

Inside the copper jacket were suspended two coils of small lead pipe, containing forty feet in all, through which water at constant temperature could be passed. One of these coils was located above and one below the prism table. The top and bottom of the air bath were made of several thicknesses of asbestos board. The bottom was perforated for the axis of the prism table, the top for two thermometers, one of which was inserted in the prism, but without touching the prism, the other between the prism and the walls of the jacket.

This air bath was supported upon a frame which was absolutely independent of the spectrometer itself, so that straining of the instrument through the very considerable weight of the air jacket could not take place.

Although, when water at constant temperature was circulated through the coils of lead pipe, the temperature of the air bath could be easily adjusted to a tenth of a degree, the two thermometers showed differences in temperature between the prism contents and the air jacket, unless the temperature of the room was very nearly that of the air bath. Under these conditions it seemed probable that the temperature of the prism contents was not uniform. These differences were traced to heat conduction through the metal standard which supported the prism. Hence all the final measurements were made in a room whose temperature was maintained constant always within 2° and usually within 0.5° of the temperature of the air bath. Even when the temperatures of the prism contents and the room differed by 2°, those of the prism and air jacket did not differ by more than three-tenths of a degree. Since the temperature of the water was obtained by means of the thermometer immersed in the water in the prism, the accuracy of the adjustment of temperature was evidently sufficient for the purpose.

The Thermometers.—The thermometers were graduated to tenths of a degree and were carefully standardized both by comparison with a thermometer calibrated by the Physikalisch-technisches Reichsanstalt, and by immersion in melting ice and melting sodium sulfate crystals.[1] Both methods gave essentially identical results.

[1] Richards and Wells, *Proc. Am. Acad.*, 38, 431 (1902).

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The Thermostat.—The water which circulated through the coils of the air jacket was brought to constant temperature by passing through a long coil of similar pipe in an electrically heated and regulated water thermostat. In order to provide a stream of water of constant velocity, the water was passed from the main first into a constant-level reservoir. Changes in temperature in the water between the thermostat and the air jacket were avoided by insulating the pipe with a layer of dry cotton.

The Water.—The water was twice distilled, once from alkaline permanganate, and once from very dilute sulfuric acid. In both distillations block-tin condensers were used, and in the final distillation the water was collected in a platinum vessel. Water prepared in this fashion has been frequently tested in this laboratory in atomic weight investigations and has been shown to be free from mineral impurities. In order that it might stand in the prism as short a period as possible, it was introduced into the prism by means of a long-stemmed funnel, after the prism had come to constant temperature in the air jacket. Although, when the water was allowed to stand in the prism, the angle of minimum deviation for sodium light slowly increased, the rate was so slow, about ten seconds in twenty-four hours, that no error from this source was to be feared, especially since less than one-half hour was normally required for a measurement and since fresh water was used for each new measurement. With a plain brass prism, and with shellac as the cement this increase in refractivity was nearly three times as rapid, while a nickel-plated prism appeared to have no advantage over brass.

That no appreciable quantity of gases was dissolved in this water was shown in one experiment by placing the prism full of water in a vacuum desiccator and exhausting. Only a few minute bubbles appeared, and the indices of refraction were found to be identical before and after this treatment.

The Light.—All adjustments, including the focusing of the collimator and telescope, and all measurements were made with sodium light. Since the difference in the index of refraction of water for the two D lines is not more than two units in the fifth decimal place, which corresponds to a difference in the angle of deviation of only five seconds, obviously the dispersion of the prism needs no consideration. The cross hair of the telescope was always set upon the least deviated side of the line, although the width of the line was too small to measure. The results can be safely assumed to apply to the average wave length of the two sodium lines, 589.3.

The Measurement of the Angle of the Prism.—The telescope and collimator were first focused for parallel rays, and were adjusted perpendicular to the axis of the instrument in the usual way. After the angle of the prism had had time to come to constancy, it was measured upon the

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spectrometer by the two common methods. By the first method the light was reflected from the collimator into the telescope from the two faces of the prism successively, the collimator and telescope being fixed and the prism rotated. In this way the supplement to the angle of the prism was determined (Method A). By the second method, the prism was fixed in position opposit the collimator, and the telescope was set upon the images of the slit as reflected from the two sides of the prism. In this way an angle double the magnitude of the angle of the prism is found (Method B). Both methods gave essentially the same results, although the accuracy of the second method is twice that of the first. Since it was possible that owing to unequal expansion the prism angle was not constant with changing temperature, measurements of the prism angle were made at various temperatures. No measurable differences could be detected even at the extreme temperatures employed. Furthermore, determinations of the prism angle were made at intervals without disclosing any variation with time.

In making the measurements, from six to ten independent settings of the telescope were made, and the average of these readings was used in the calculations. In only a very few cases was the extreme variation of these readings as much as ten seconds. Fresh observations were then made on different portions of the divided circle.

The Measurement of the Angle of Minimum Deviation.—The prism was first leveled and allowed to come to the temperature of the air jacket. Next it was filled with water as described, and after it had been set at the angle of minimum deviation, the cross hair of the telescope was set upon the sodium line and its position read. After the series of readings of this position had been made, the prism was removed and the direct reading was obtained in the same way. Thus, disturbance of the telescope during the adjustment of the prism was avoided. The operations were then repeated on several different portions of the divided circle.

The Results.—The index of refraction was calculated according to the well known formula,

$$n = \frac{\sin \tfrac{1}{2}(D + A)}{\sin \tfrac{1}{2} A},$$

where D represents the angle of minimum deviation and A is the refracting angle of the prism. A positive error of ten seconds in the determination of the refracting angle of the prism produces a difference in the index of refraction of —0.00002, while a positive error of ten seconds in the determination of the angle of minimum deviation produces a difference of +0.00004 in the refractive index. Assuming a maximum error in each reading of five seconds, the total maximum error in the refractive index is thus 0.00003. That the error was actually no larger

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than this was evident from the close agreement of the readings in each series, each successive series having been made after the removal of one of the glass plates from the prism and a redetermination of the prism angle.

The angular values recorded in Table I were obtained as follows:[1] From the two vernier readings with the telescope in the position of minimum deviation were subtracted the corresponding two direct readings, and the two differences were averaged. Each angle in the table is the average of from four to nine such average differences, the extreme variations of which were never over eight seconds and usually less than five seconds. The magnitude of the prism angle was found in a similar way.

TABLE I.

SERIES I.

Prism angle, Method A	60° 10′ 52″
Method B	60° 10′ 54″
Average	60° 10 53″

Temperature	20°	25°	30°
Angle of deviation	23° 41′ 32″	23° 39′ 9″	23° 36′ 32″
Index of refraction	1.33297	1.33246	1.33189

SERIES II.

Prism angle, Method B 60° 12′ 37″

Temperature	20°	25°
Angle of deviation	23° 42′ 44″	23° 40′ 17″
Index of refraction	1.33302	1.33249

SERIES III.

Prism angle, Method A	(21° C.) 60° 7′ 40″
Method B	(21° C.) 60° 7′ 39″
Method B	(30° C.) 60° 7′ 39″
Average	60° 7′ 39″

Temperature	20°	25°
Angle of deviation	23° 39′ 48″	23° 37′ 28″
Index of refraction	1.33298	1.33248

SERIES IV.

Prism angle, Method A	(30° C.) 60° 3′ 28″
Method B	(23° C.) 60° 3′ 31″
Method B	(30° C.) 60° 3′ 31″
Average	60° 3′ 30″

Temperature	20°	25°	30°
Angle of deviation	23° 37′ 35″	23° 35′ 13″	23° 32′ 35″
Index of refraction	1.33300	1.33248	1.33191

[1] The following experiments were made by L. L. Burgess.

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SERIES V.

Prism angle, Method A		(27° C.) 60° 2′ 19″	
Method B		(27° C.) 60° 2′ 21″	
Average		60° 2′ 20″	
Temperature	.....	.....	30°
Angle of deviation	.....	.....	23° 31′ 55″
Index of refraction	.....	.....	1.33191
Temperature	20°	25°	30°
Average index of refraction	1.33299	1.33248	1.33190

It is interesting to compare these results with those of earlier experimenters. The following data, which are taken from the tables of Landolt-Börnstein-Meyerhoffer, are in many cases corrected to the temperature in question, the observations having been obtained at slightly lower or higher temperatures. The averages agree very closely with ours at the same temperatures.

		20°.	30°.
1856	Jamin	1.33300	1.33191
1867	van der Willigen	1.33304	...
1867	Rühlmann	1.33295	1.33200
1876	Wiedermann	1.33291	...
1880	Lorenz	1.33301	1.33203
1885	Dufet	1.33292	1.33186
1885	Kanonnikoff	1.33310	...
1888	Ketteler	1.33294	1.33188
1889	Schütt	1.33300	...
1890	Bender	1.33287	...
1890	Buchkremer	1.33313	...
1891	Brühl	1.33304	...
1891	Röntgen and Zehnder	1.33304	1.33194
1892	Walter	1.33299	...
1893	Ruoss	1.33300	...
1894	Simon	1.33306	...
1894	Verschaffelt	1.33299	1.33196
1903	Flatow	1.33300	...
	Average	1.33300	1.33194

As a check upon the accuracy of these determinations, comparisons of the indices of refraction of water at the three temperatures investigated were made with the Pulfrich refractometer used in the work described in the following paper. The prism and cylinder of this instrument were provided with water jackets through which a stream of water at the desired temperature could be passed. Differences in the angle of emergence could be read by means of a micrometer to 0.1′. Differences in index of refraction corresponding to the differences in the readings could be found in tables furnished with the instrument.

The method of experimentation was to allow the temperature of the prism and cylinder to become constant at the desired point. Then the

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cylinder was partly filled with the purest water and after its temperature had become constant several readings of the instrument with sodium light were taken. The water in the cylinder was several times replaced by a fresh portion without ever producing an appreciable difference in reading.

The following differences in the angle of emergence were found in two entirely separate sets of readings, each difference representing from twelve to twenty closely agreeing observations.[1] The first set of readings was made in an ordinary laboratory in which the temperature fluctuated between 20 and 25°. The second set was made in a room maintained very nearly at the temperature in question.

TABLE II.

	20–25°.	25–30°.
I	6.2′	7.6′
II	6.4′	7.5′
Average	6.3′	7.6′

Since with the refractometer employed a difference in the angle of emergence of 1.0′ corresponds to a difference in index of refraction of 0.000077 in the case of a substance having the refractive power of water, the above differences in the angle of emergence correspond to differences in the index of refraction of

$$20\text{–}25° \quad 6.3 \times 0.000077 = 0.000485$$
$$25\text{–}30° \quad 7.6 \times 0.000077 = 0.000585$$

Furthermore, owing to change in the index of refraction of the glass of the prism itself with changing temperature, a positive correction of 0.0000034 per degree is necessary. The corrected values are as follows:

$$20\text{–}25° \quad 0.000485 + 0.000017 = 0.00050$$
$$25\text{–}30° \quad 0.000585 + 0.000017 = 0.00060$$

These differences correspond as closely as could be expected with the corresponding differences obtained by the spectrometer method, 0.00051 and 0.00058.

In order to correct to vacuum the indices in the table on page 898, which are of course referred to air at the same temperature, each value must be multiplied by the index of refraction of air at that temperature, referred to vacuum.

$$20° \quad 1.33299 \times 1.000272^2 = 1.33335$$
$$25° \quad 1.33248 \times 1.000267^2 = 1.33284$$
$$30° \quad 1.33190 \times 1.000262^2 = 1.33225$$

From the corrected values the specific refraction of water may be calculated by any of the formulas which have been proposed for the purpose. This has been done with the use of the Gladstone and Dale[3]

[1] These experiments were made by H. W. Daudt.

[2] Landolt-Börnstein-Meyerhoffer, 689.

[3] *Phil. Trans.*, 1858, p. 887.

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and the Lorentz[1] and Lorenz[2] formulas. Values for the density of water are taken from the tables of Landolt-Börnstein-Meyerhoffer.

Temperature.	$\frac{n-1}{d}$.	$\frac{n^2-1}{n^2+2}\frac{1}{d}$.
20°	0.333941	0.206256
25°	0.333818	0.206209
30°	0.333694	0.206167

The specific refraction is not constant in either case, diminishing regularly with increasing temperature.[3] The temperature coefficient is smaller in proportion to the magnitude of the specific refraction in the case of the Lorentz and Lorenz formula. The difference between two successive values of the specific refraction correspond to a difference of 0.00007 in the index of refraction in the case of the Lorentz and Lorenz formula, and of 0.00012 in the case of the Gladstone and Dale formula, while the values for the index of refraction found in this investigation are probably correct within 0.00002.

As the result of this research the index of refraction of water for sodium light at three temperatures is found to be:

	Referred to air at the same temperature.	Referred to vacuum.
20°	1.33299	1.33335
25°	1.33248	1.33284
30°	1.33190	1.33225

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE REFRACTIVE POWER OF THE HALOGEN SALTS OF LITHIUM, SODIUM AND POTASSIUM IN AQUEOUS SOLUTION.

BY GREGORY P. BAXTER, ARTHUR C. BOYLSTON, EDWARD MUELLER, N. HENRY BLACK AND PHILIP B. GOODE

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The refractive power of aqueous solutions of electrolytes has been the subject of numerous researches by many investigators,[4] and attention has been called to several kinds of regularities. One sort concerns the change in index of refraction of the solution with changing concentration. Another concerns the more or less close application of the Law of Mixtures to the specific refractions of the components of the solution and that of the solution. Still a third regularity has very recently been pointed out by Chéneveau and concerns the change in the index of refraction of the solvent alone as it is diluted with solute.

[1] *Wied. Ann.*, 9, 642.

[2] *Ibid.*, 11, 77 (1880).

[3] Concerning the change in specific refraction with the temperature in the case of organic substances see Falk, THIS JOURNAL, 31, 86 (1909).

[4] For a very complete bibliography of the subject see Chéneveau, *Ann. chim. phys.*, 8th Series, 12, 384 (1907).

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With regard to the first sort of regularity, it is well recognized that the index of refraction of a solution of an electrolyte does not increase at the same rate as either the percentage composition or the concentration. This is due, in part at least, to the fact that when a salt is dissolved in water the contraction or expansion during solution per unit quantity of salt varies with the concentration of the solution. It is pointed out in a following paper that there is good reason for believing that this varying expansion or contraction during solution is closely connected with electrolytic dissociation, and hydration. In any case, in comparing the indices of refraction of solutions of different substances, it is most reasonable to select solutions of the same degree of dissociation.

Bender[1] first showed that with dilute solutions of electrolytes, where the degree of dissociation is large, the increments of refractive index with changing concentration, if referred to molecular quantities of salt, show distinct additive relationships. This is of course to be expected if the property is ionic rather than molecular. The additive relationships would be most satisfactory at infinit dilution, but the difficulty in obtaining sufficiently accurate measurements makes the comparison less satisfactory with very dilute solutions.

The second sort of regularity, which serves to connect index of refraction and density, concerns the specific refractions of the solutions of electrolytes and of their components. Of the various expressions for specific refraction in common use, the best known and the most satisfactory from a general standpoint are those of Gladstone and Dale,[2] and Lorentz[3] and Lorenz,[4] $\frac{n-1}{d}$ and $\frac{n^2-1}{n^2+2}\frac{1}{d}$, respectively. The second of these two is in general more nearly a constant under varying conditions. It is to be noted, however, that neither expression remains exactly a constant with changing temperature[5] and that *at present there is no wholly satisfactory general expression connecting change of index of refraction with changing density*. Hence any relationship which depends upon specific or molecular refraction is more or less uncertain.

The Law of Mixtures has been found first by Biot and Arago to hold for the specific refractions of solutions and their components, *i. e.*, the following equation holds very closely although not exactly true:

$$k_e x + k_w (100 - x) = k_s 100,$$

where k_e, k_w and k_s represent the specific refractions of solute, solvent

[1] *Wied. Ann.*, 39, 89 (1890). See also Valson, *Jahresb. Chem.*, 1873, 135.
[2] *Phil. Trans.*, 1858, 887.
[3] *Wied. Ann.*, 9, 642 (1880).
[4] *Ibid.*, 11, 70 (1880).
[5] See especially Falk, THIS JOURNAL, 31, 86 (1909); also Baxter, Burgess and Daudt, preceding paper.

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and the solution, respectively, and x represents the per cent. of solute.

Upon the assumption that the specific refraction of the solvent in the solution does not change with changing concentration and is equal to that of pure solvent at the same temperature, the specific refraction of the solute can be calculated from that of the solution. The results so obtained for the specific refraction of an electrolyte are not absolutely constant with changing concentration, the differences being usually ascribed to the salt itself. To ascribe all the differences to the salt alone is, however, a somewhat questionable method of procedure, since during the solution and dissociation of an electrolyte deep-seated changes in both solute and solvent undoubtedly take place. Even upon the above assumption the change in the specific refraction of the electrolyte with changing concentration is not very large, and interesting additive relationships have been obtained by comparison of the molecular refractions of different electrolytes, the latter values being obtained by multiplying the specific refractions by the molecular weights. It is interesting to note that the molecular refractions of electrolytes in aqueous solution, when compared with the corresponding values calculated from the index of refraction and the density of the solid, where the latter is either amorphous or isotropic, show in most cases considerable differences.

Chéneveau's[1] method of determining the change in the index of refraction of the water by the electrolyte also depends upon the assumption of a constant specific refraction of water, and offers no special advantages over the Law of Mixtures.

Although the experimental work upon which the previous considerations have been based has in isolated cases been very carefully carried out, in the majority of instances not only is there no assurance that such is the case but there is evidence that certain precautions necessary for very accurate work were omitted. Consequently some uncertainty exists as to the exactness with which the various relationships hold even for the simpler substances. The physical measurements of index of refraction and density are comparatively easy to make with a high degree of accuracy. On the other hand, since frequently little care seems to have been taken to ensure freedom of the substances employed from probable impurities, especially from moisture, many determinations of concentration are open to suspicion. The object of the present investigation was to repeat with considerable care some of the earlier experimental work. For the sake of comparison, the salts examined include a few which have already been very carefully investigated.

The halogen compounds of the alkalis were chosen for examination because of certain distinct advantages which they seemed to offer. In the first place, the molecular structure of these salts seems to be as simple

[1] *Loc. cit.*

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as any, and is surely similar. Hence constitutive irregularities such as are manifested by isomeric organic derivatives are undoubtedly at a minimum. In the second place, these salts are all highly dissociated in aqueous solution, and to essentially the same extent at equivalent concentrations. The proportion of the salt in the ionic condition being consequently high, even at considerable concentrations, the excess of the solution over water in refractive power is due largely to the combined effects of cations and anions. Constitutive influences within the molecule being able to affect only a portion of the total quantity of electrolyte, additive relationships are to be expected to hold as closely in this series of electrolytes as in any.

One of the chief differences between the salts in question lies in the fact that, although *hydrolysis* is surely very slight at ordinary temperatures, *hydration* both of ions and of molecules undoubtedly exists, and to various degrees. Washburn,[1] for instance, has shown that the relative hydrations of the lithium, sodium, and potassium ions referred to the chlorine ion as unity, are 4.3, 2.0, and 1.3 in normal solution at 25°. Furthermore, there is good reason for believing that the chlorine ion is more and the iodine ion less hydrated than the bromine ion.[2] With regard to the hydration of the molecules, the situation is less certain. But if crystal water may be considered a measure of the extent of molecular hydration, lithium salts are most and potassium least hydrated.

Purification of Materials.

Hydrochloric Acid.—The hydrochloric acid used in the preparation of all the chlorides was the commercial chemically pure article, once distilled.

Hydrobromic Acid.—In the case of the hydrobromic acid used in the preparation of the bromides, more elaborate precautions were taken to eliminate traces of chlorine and iodine usually contained in hydrobromic acid made from commercial bromine, since mere crystallization of bromides does not free them at all rapidly from chlorides and iodides. The removal of chlorine was secured by distilling the bromine three times from a solution of a bromide. In each distillation the bromide was made from a portion of the product of the previous distillation.[3] Iodine was eliminated by boiling with an excess of free bromine a solution of a bromide made from the product. The purified bromine was either used directly, after distillation, or was converted into hydrobromic acid with hydrogen sulfide and water. The solution of hydrobromic acid was

[1] THIS JOURNAL, 31, 322 (1909).

[2] For a critical review of the subject of hydration see Washburn, *Technology Quarterly*, 21, 360 (1909).

[3] Richards and Wells, *Proc. Am. Acad.*, 41, 440 (1996); Baxter, *Ibid.*, 42, 202 (1906).

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freed from sulfur and bromide of sulfur by filtration and the traces of sulfuric acid formed during the action of the bromine on the hydrogen sulfide were eliminated by precipitation in moderately dilute solution with recrystallized barium hydroxide. The acid was then twice distilled, the second distillation being with a quartz condenser.

Hydriodic Acid.—Hydriodic acid was prepared by methods very similar to those used in the purification of the hydrobromic acid.[1] The greater part of the chlorine and bromine was removed from commercial iodine by initial distillation from solution in aqueous potassium iodide. Then the product was twice reduced to hydriodic acid by hydrogen sulfide and water, and the solution of hydriodic acid, after prolonged boiling to remove hydrocyanic acid resulting from impurity of cyanogen in the original iodine,[2] was partially oxidized to iodine with a slight excess of recrystallized potassium permanganate. The resulting iodine was finally again reduced with hydrogen sulfide, the suspended sulfur was removed from the hydriodic acid solution by filtration, and the hydriodic acid was twice distilled, once with a still and condenser made entirely of glass, and once with a quartz condenser. Although the acid was colored strongly with free iodine, in the crystallization and fusion of the salts made from the acid the iodine was completely removed.

Lithium Chloride.—In the purification of the lithium salts commercial lithium carbonate was the starting point of all the pure material. It was found advantageous first to wash the carbonate by decantation with water, since a considerable portion of the more soluble carbonates could be extracted in this way. In the preparation of lithium chloride the carbonate was next dissolved in hydrochloric acid and reprecipitated with an excess of ammonium carbonate and ammonia. After thorough washing with water the carbonate was again dissolved in hydrochloric acid and the salt was several times recrystallized from a solution strongly acid with hydrochloric acid. The product was free from all but spectroscopic traces of sodium.

Lithium Bromide and Iodide.—In the preparation of lithium bromide and iodide the washed carbonate was first dissolved in nitric acid and the lithium nitrate was three times crystallized to eliminate chlorides as well as metallic impurities. The third crop of crystals was essentially free from sodium. Lithium carbonate was then precipitated from the purified nitrate by means of ammonium carbonate and the lithium carbonate washed until the wash waters were free from nitrate. Finally the carbonate was dissolved in either hydrobromic or hydriodic acid and the bromide and iodide were recrystallized at least three times.

Since the precipitation of lithium carbonate by ammonium carbonate

[1] Baxter, *Proc. Am. Acad.*, 40, 419 (1904).

[2] Richards and Singer, *Am. Chem. J.*, 27, 205 (1902).

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always involves a very considerable loss of material, owing to the solubility of lithium carbonate in solutions of ammonium salts, other methods of purification were attempted. Of these, one of the most effective was the solution of the carbonate in a solution of carbonic acid and subsequent precipitation by boiling, although it is best suited for the treatment of small quantities of material.

Sodium Chloride.—Sodium chloride was purified by twice precipitating the salt from aqueous solution by means of hydrochloric acid gas.

Sodium Bromide and Iodide.—Sodium bromide and iodide were prepared by dissolving the purified carbonate in pure hydrobromic and hydriodic acids, respectively. The carbonate itself had been three times recrystallized to free it from other alkali impurities and salts of sodium.[1] Finally the bromide and iodide were three times recrystallized.

Potassium Chloride.—Potassium chloride was purified in the same fashion as in the case of sodium chloride, by double precipitation with hydrochloric acid.

Potassium Bromide.—For the preparation of potassium bromide, potassium oxalate was three times recrystallized, until free from chloride, and was converted into the bromide by the cautious addition of a slight excess of bromine.[2] The potassium bromide was finally several times crystallized.

Potassium Iodide.—Potassium iodide was prepared by the action of pure hydriodic acid on potassium bicarbonate which had been freed from sodium by crystallization from aqueous solution.[3] The salt was then purified further by crystallization.

In the preparation of all these salts platinum vessels were largely employed, especially in the later stages of the purifications. Crystals were separated from mother liquor by centrifugal drainage with a centrifugal machine provided with platinum baskets and receivers. All the water was doubly distilled, once from alkaline permanganate and once from very dilute sulfuric acid, with the use of block tin condensers in both distillations. When tested spectroscopically the salts gave indications of great purity. Their solutions were perfectly clear. There seemed every reason to believe that the quality of the material was more than sufficient for the purpose.

As has been strongly emphasized by Richards,[4] one of the most important precautions in preparing a definit quantity of salt for exact work is that of fusing the substance in order to eliminate last traces of moisture. This precaution was observed in all cases.

[1] Richards and Wells, THIS JOURNAL, 27, 471 (1905).
[2] Richards and Mueller, *Ibid.*, 29, 664 (1907).
[3] Baxter and Brink, *Ibid.*, 30, 50 (1908).
[4] *Z. physik Chem.*, 46, 189 (1903).

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In the case of sodium and potassium chlorides, which show no tendency to become basic when fused even in moist air, the fusion was carried out in platinum crucibles or dishes, and the salt was weighed out from ordinary weighing bottles to which the salts had been transferred immediately after fusion. Although Richards and Wells[1] and Richards and Stähler[2] have shown that sodium and potassium chlorides containing traces of hydrochloric acid, when fused in platinum vessels attack the platinum slightly, the impurity introduced in this way must have been very small, since no perceptible amount of platinum could be detected in either the fused salt or in its aqueous solution.

Lithium chloride, on the other hand, possesses the above disadvantage of becoming basic when fused in air, while in addition it is very hygroscopic and correspondingly difficult to weigh. Hence this salt was first fused in a platinum boat in a current of dry nitrogen and hydrochloric acid gases,[3] and the boat was weighed in a glass weighing bottle to which it had been transferred without exposure to moist air,[4] after the hydrochloric acid gas had been displaced by dry nitrogen and this in turn by dry air. The nitrogen had been prepared by the method of Wanklyn by passing air charged with an excess of ammonia over hot copper and removing the excess of ammonia with sulfuric acid, first dilute, then concentrated. In a recent private communication, Dr. R. C. Wells has called our attention to the fact that nitrogen made in this way usually contains appreciable amounts of hydrogen, resulting from the catalytic decomposition of the excess of ammonia in contact with the hot copper. This hydrogen could have had no injurious effect upon either the lithium chloride or the bromides and iodides of all three alkalis, which also were fused in an atmosphere containing nitrogen.

The three bromides were prepared for weighing in much the same way that the lithium chloride was prepared, by fusion in a current of pure dry nitrogen and hydrobromic acid gases.[5] After the fusion of the salt, the hydrobromic acid gas was displaced by nitrogen and the nitrogen in turn by dry air, before the boat was transferred to the weighing bottle in which it was weighed. The fused bromides were perfectly clear and yielded exactly neutral aqueous solutions.

In the case of the iodides, fusion was carried out in a current of pure dry nitrogen. Since lithium iodide, when fused under these conditions becomes somewhat basic, a small proportion of pure ammonium iodide

[1] THIS JOURNAL, 27, 463 (1905).

[2] *Ibid.*, 29, 630 (1907).

[3] For a description of the apparatus and the purification of the gases see Baxter and Hines, THIS JOURNAL, 27, 226 (1905).

[4] Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

[5] For a description of the apparatus for the preparation and purification of the gases, see Baxter, *Proc. Am. Acad.*, 39, 246 (1903).

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was added to the salt before fusion, and the greater part of the water of crystallization was carefully expelled before the volatilization of the ammonium iodide. In this way the alkalinity of the fused salt, although only in one case entirely eliminated, was reduced to a quantity corresponding to less than two-tenths of a milligram of lithium hydroxide in every case, and usually to less than one-tenth of a milligram. Each solution of lithium iodide was tested for ammonium salts with Nessler's solution, with negative results in all cases.

The potassium and sodium iodides, when fused in nitrogen, gave neutral solutions.

After the salt had been dried and weighed, the boat and salt were placed in a stout flask and the salt was dissolved in the minimum amount of water. The solution was then quantitatively transferred to a graduated flask. When very small flasks were employed it was sometimes necessary to evaporate slightly the rinsings of the solution flask. This evaporation was carried out on a steam bath in a platinum dish carefully protected from dust and fumes. Next the flask was filled nearly to the graduation with freshly distilled water at the desired temperature and the solution was thoroughly shaken in order to avoid subsequent change of volume in mixing. Then the flask was immersed in a water thermostat maintained at 25° and was allowed to remain in the thermostat for from two to six hours, according to the size of the flask, until constant temperature was reached. The volume of the solution was adjusted exactly to the graduation while the flask remained in the thermostat. Finally the solution was very thoroughly mixed by shaking, and the flask with contents, after being carefully dried with a clean cloth and allowed to come nearly to the temperature of the balance room, was weighed.

The flasks were of various sizes, from 35 cc. to 1000 cc., the smaller flasks being employed for the more concentrated, the larger for the less concentrated solutions. The greater accuracy necessary in determining the composition and density of the less concentrated solutions was thus more easily attained. The necks of the flasks were considerably constricted at the point of graduation, in order to make possible more accurate adjustment of the volume of the solution. The flasks were always weighed by substitution, the smaller flasks upon a balance sensitive to one-tenth of a milligram, the larger upon one sensitive to two milligrams. The true volumes of the flasks at 25° were determined by weighing them filled with pure water, the volume of the apparent gram of water being assumed to be 1.00400 cc. at 25°.

In some instances solutions were prepared by dilution to definit volume of a weighed amount of a stronger solution, and in the case of a few of the most concentrated solutions the salt was not weighed before

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dissolving, but the composition of the solution was determined by analysis for halogen by precipitation of the silver halide. These exceptions are noted in the tables of results.

The salts themselves were weighed on a very sensitive Troemner balance with weights standardized in the fashion described by Richards.[1]

All weights, both of salts and of solutions, were corrected to the vacuum standard, the following quantities being added for each gram of salt:

LiCl.....	+0.00044	LiBr.....	+0.00021	LiI.....	+0.00015
NaCl.....	+0.00042	NaBr.....	+0.00025	NaI.....	+0.00019
KCl.....	+0.00046	KBr.....	+0.00029	KI.....	+0.00024

The measurements of the indices of refraction of the solutions were made with an improved form of Pulfrich refractometer[2] manufactured by Zeiss of Jena. This instrument is provided with a vernier enabling the observer to read the angle of emergence of the ray of grazing incidence with an accuracy of 0.5′. The correction of the scale was found by determining the reading for pure water and comparing this reading with that interpolated for the index of refraction of water from the tables furnished with the instrument, the index of refraction of water for sodium light at 25° being assumed to be 1.33248.[3] The difference between the reading actually observed and that interpolated from the table was used as a correction for the scale. The accuracy of the index of refraction for observations made in this way is about four units in the fifth decimal place. The instrument is further provided with a micrometer attachment by means of which differences of less than five degrees between the angles of emergence for two liquids can be determined with an accuracy of 0.1′. The readings of the micrometer were found to correspond exactly with graduations of the divided circle in the neighborhood of the reading for pure water. In the examination of the more dilute solutions this micrometer was employed, the difference between the reading for pure water and that for the solution being subtracted from the interpolated reading for water. An accuracy as great as two in the fifth decimal place of the index of refraction was thus obtained. With most solutions for which the readings of the refractometer differed from that of water by less than five degrees the latter method was employed. Although the tables furnished with the instrument apply at 20° both of the above methods of comparison with water obviate the necessity of applying a temperature correction. The temperature correction for the prism of the instrument is, however, only 0.0000034 per degree.

Both the cell and the prism of the refractometer were provided with

[1] THIS JOURNAL, 22, 144 (1900).

[2] *Z. physik. Chem.*, 18, 294 (1895).

[3] Baxter, Burgess and Daudt, see preceding paper.

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devices for maintaining constant temperature by means of water circulation, a surrounding jacket in the case of the prism and a hollow silver plunger in the case of the cell. Water flowed from a large constant level reservoir through a twelve-meter coil of small lead pipe in a thermostat, and thence through a short insulated tube to the water jacket of the refractometer. Even with cold water flowing through the lead coil the temperature of the thermostat remained constant within five one-hundredths of a degree. After the current of water had flowed through the jackets of the refractometer for a few moments no important difference in temperature could be detected by means of thermometers, one of which was placed in the thermostat and the other in the plunger dipping into the cell of the refractometer. Since a difference in temperature of one-tenth of a degree is necessary to produce a change in the index of refraction of water of one unit in the fifth decimal place, the adjustment of temperature was evidently sufficiently exact.

Both thermometers were carefully compared with one standardized by the Physikalisch-Technisches Reichsanstalt.

Observations with all the solutions were made with sodium light. For the present purpose this light is essentially homogeneous, since the difference in index of refraction of water for the two yellow rays of sodium light is only two in the fifth decimal place.

After the introduction of each solution into the dried cell of the refractometer and the immediate closing of the cell by means of the plunger, which was made to fit tightly around the rim of the cell by means of a rubber ring in order to avoid evaporation of the solution, the temperature of the solution was allowed to come to constancy at 25°. Next the reading of the instrument was taken. The solution in the cell was then several times replaced with a fresh sample by means of a pipet, readings being taken in each case as soon as the temperature became constant. These readings seldom varied as much as 0.3′. The index of refraction corresponding to the average of the readings with each solution is given in the tables.

The weight of salt, the weight of the solution and the volume of the solution being known, the per cent. of salt and the specific gravity of the solution referred to water at 4° were calculated. Upon the assumption that the specific refractions of the salt and the water are additive, the specific and molecular refractions of the salt were computed by equations I and II, respectively:

$$\text{I.} \qquad k = \frac{1}{p}\left(\frac{(n_s^2-1)}{(n_s^2+2)}\,\frac{100}{d_s} - \frac{(n_w^2-1)}{(n_w^2+2)}\,\frac{(100-p)}{d_w}\right)$$

$$\text{II.} \qquad Mk = \frac{M}{p}\left(\frac{(n_s^2-1)}{(n_s^2+2)}\,\frac{100}{d_s} - \frac{(n_w^2-1)}{(n_w^2+2)}\,\frac{(100-p)}{d_w}\right)$$

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in which

k = specific refraction of the salt in solution;
M = molecular weight of the salt;
p = per cent. of salt;
n_s = index of refraction of the solution at 25°;
n_w = index of refraction of water at 25°;
d_s = density of the solution at 25°;
d_w = density of water at 25°.

In calculating molecular weights, values referred to silver 107.88 are employed as follows:

Li.....	6.94	Na.....	23.00	K.....	39.10
Cl.....	35.46	Br.....	79.92	I.....	126.92

As stated before, the refractive index of water is assumed to be 1.33248 at 25°. It is to be noted, however, that the method of standardizing the refractometer by comparison with pure water makes the final result for the molecular refraction of the salt independent of a small error in the refractive index of water. The density of water at 25° is assumed to be 0.997071. Since this value was used in the standardizing of the graduated flasks, the calculated molecular refraction of the salt is essentially independent of a small error in this value also.

In the following tables the values for index of refraction are referred to air. They may be referred to vacuum in the usual way by multiplying by the refractive index of air referred to vacuum, the latter value being 1.000265 at 25° and normal pressure. Since in each experiment the reading for pure water was always taken shortly before the reading for the solutions the effect of variation in the density of the air upon the index of refraction of air referred to a vacuum has no effect upon the corrected index of refraction of the solution and hence upon the molecular refraction. Since, however, the effect upon the calculated specific refraction of the salt of correcting the indices of refraction of water and the solution to vacuum is very slight, as the following table shows,

Salt.	Concentration. Per cent.	Specific refraction uncorrected.	Specific refraction corrected to vacuum.
NaBr.....	1	0.1235	0.1235
	17	0.12444	0.12448
	46	0.12368	0.12374
LiCl.....	13	0.20448	0.20456

this correction is omitted in the calculations of the refractive constants.

The following tables give for each salt and each solution investigated, w_s, the weight of salt in grams in vacuum; w_l, the weight of solution in grams in vacuum; p, the per cent. of salt in solution; m, the gram molec-

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ular concentration of salt per liter; d, the density of the solution; n, the index of refraction of the solution for sodium light; k, the specific refraction of the salt; and Mk, the molecular refraction of the salt.

It is to be noted that the specific and molecular refractions are much more highly sensitive to experimental differences in the case of dilute solutions than in the case of concentrated solutions. For instance, with a one per cent. solution of sodium bromide a difference of 0.00001 in the refractive index makes a difference of 0.3 per cent. in the molecular refraction of the salt, and a difference in the density of 0.0001 produces a difference of 1.4 per cent. in the molecular refraction. On the other hand, with a seventeen per cent. solution similar differences in the measurements produce differences in the molecular refraction of only 0.03 and 0.08 per cent., respectively. An error of one-tenth of one per cent. in the concentration of the solution produces an error of 0.07 per cent. in the molecular refraction no matter what the actual concentration.

Unless otherwise stated, the experimental work was performed by A. C. Boylston.

TABLE I.—LITHIUM CHLORIDE.

M = 42.40.

w_s.	w_l.	p.	m.	d.	n.	k.	Mk.
1.5684	250.78	0.6254	0.1477	1.00068	1.33388	0.2093	8.88[1]
1.7524	251.155	0.6977	0.1648	1.00116	1.33405	0.2115	8.97
2.3459	251.466	0.9329	0.2206	1.00240	1.33456	0.2134	9.05
2.4061	251.22	0.9578	0.2265	1.00243	1.33446	0.2066	8.76[1]
2.4333	251.17	0.9688	0.2292	1.00271	1.33460	0.2088	8.86[1]
3.5588	252.148	1.4114	0.3347	1.00511	1.33555	0.2106	8.93
2.8123	101.716	2.7648	0.6608	1.01308	1.33833	0.2052	8.70[1]
7.0410	254.153	2.7703	0.6621	1.01311	1.33842	0.2068	8.77
5.9308	103.411	5.7352	1.393	1.02966	1.34465	0.2073	8.79
6.8558	103.931	6.5965	1.610	1.03484	1.34653	0.2071	8.78
11.2518	106.289	10.5860	2.643	1.05832	1.35494	0.2049	8.69
14.1275	107.762	13.1099	3.315	1.07299	1.36024	0.2045	8.67

TABLE II.—SODIUM CHLORIDE.

M = 58.46.

w_s.	w_l.	p.	m.	d.	n.	k.	Mk.
5.2938	1002.54	0.5280	0.0904	1.00079	1.33342	0.1605	9.38
5.5077	1002.73	0.5493	0.0940	1.00098	1.33341	0.1545	9.03
10.0384	1005.88	0.9980	0.1715	1.00413	1.33417	0.1558	9.11
1.0674	100.301	1.0618	0.1825	1.00432	1.33433	0.1628	9.52
5.5737	503.59	1.1068	0.1903	1.00477	1.33438	0.1592	9.31
5.5357	103.352	5.3562	0.9486	1.03488	1.34169	0.1584	9.26
5.5969	103.396	5.4131	0.9591	1.03532	1.34179	0.1582	9.23
6.1128	42.616	14.344	2.704	1.10146	1.35747	0.1582	9.23

[1] Experiment by P. B. Goode, the remainder by N. H. Black.

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TABLE III.—POTASSIUM CHLORIDE.

M = 74.56

w_s.	w_l.	p.	m.	d.	n.	k.	Mk.
9.5104	1004.79	0.9466	0.1274	1.00303	1.33376	0.1544	11.51[1]
0.9790	100.76	0.9716	0.1307	1.0031	1.33380	0.1550	11.56
2.4558	251.38	0.9769	0.1315	1.0032	1.33380	0.1520	11.34
5.0204	502.89	0.9983	0.1344	1.00337	1.33382	0.1514	11.29[1]
2.5179	251.46	1.0013	0.1348	1.0036	1.33388	0.1516	11.31
2.4705	101.68	2.4297	0.3299	1.0122	1.33577	0.1539	11.48
2.5042	101.70	2.4623	0.3344	1.0124	1.33581	0.1539	11.48
23.9109	514.50	4.6474	0.6398	1.02654	1.33871	0.1518	11.33[1]
4.9785	103.31	4.8150	0.6648	1.0285	1.33896	0.1500	11.19
4.9898	103.27	4.8318	0.6663	1.0281	1.33896	0.1505	11.22
4.9926	103.28	4.8340	0.6667	1.0282	1.33896	0.1500	11.19
7.4973	104.75	7.1573	1.0012	1.0428	1.34215	0.1522	11.35
7.5119	104.77	7.1699	1.0031	1.0430	1.34215	0.1518	11.32
9.5598	105.96	9.0221	1.277	1.0549	1.34463	0.1523	11.36
10.0038	106.25	9.4153	1.340	1.0577	1.34517	0.1517	11.31
10.0394	105.685	9.5004	1.349	1.05814	1.34528	0.1520	11.34[1]
15.017	109.15	13.758	2.005	1.0865	1.35122	0.1527	11.39
15.022	109.21	13.755	2.006	1.0872	1.35122	0.1517	11.31
20.003	112.05	17.852	2.671	1.1155	1.35678	0.1514	11.29
20.063	112.10	17.898	2.679	1.1160	1.35687	0.1510	11.27
24.701	114.77	21.522	3.299	1.1426	1.36202	0.1508	11.25
25.018	114.92	21.770	3.341	1.1441	1.36238	0.1513	11.28

TABLE IV.—LITHIUM BROMIDE.

M = 86.86.

w_s.	w_l.	p.	m.	d.	n.	k.	Mk.
0.1982	100.09	0.1980	0.0228	0.9984	1.33273	0.1370	11.90[2]
0.3335	100.20	0.3328	0.0383	0.9995	1.33300	0.1418	12.32[2]
0.3898	100.24	0.3889	0.0449	0.9999	1.33307	0.1412	12.27
0.4324	100.26	0.4313	0.0496	1.0001	1.33309	0.1409	12.24[2]
0.8179	100.53	0.8136	0.0939	1.0028	1.33369	0.1440	12.51[2]
1.0314	100.69	1.0244	0.1184	1.0044	1.33401	0.1427	12.40
1.4443	100.613	1.4355	0.1665	1.00745	1.33466	0.1427	12.40
1.6999	101.17	1.6802	0.1952	1.0092	1.33499	0.1419	12.32
0.9492	50.71	1.8718	0.2179	1.0108	1.33530	0.1400	12.16
1.8296	51.34	3.5637	0.4198	1.0233	1.33788	0.1407	12.22
1.8442	51.343	3.5919	0.4232	1.0234	1.33793	0.1416	12.30
1.9285	51.40	3.7527	0.4427	1.0245	1.33825	0.1430	12.42
2.2189	51.61	4.2994	0.5092	1.0287	1.33905	0.1417	12.31
2.3906	51.72	4.6222	0.5486	1.0309	1.33954	0.1427	12.40
3.2410	52.325	6.1940	0.7441	1.04335	1.34200	0.1408	12.23
8.3797	55.99	14.966	1.922	1.1153	1.35662	0.1405	12.20
10.4304	57.340	18.190	2.395	1.14337	1.36254	0.1415	12.29
11.397	35.015	32.55	4.829	1.2889	1.39194	0.1407	12.22[3]

[1] Experiment by A. C. Boylston, the remainder by E. Mueller.

[2] Diluted from a more concentrated solution.

[3] Analyzed by precipitation of the bromine as silver bromide.

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TABLE V.—SODIUM BROMIDE.

M = 102.92.

ws.	*wl.*	*p.*	*m.*	*d.*	*n.*	*k.*	M*k.*
0.4873	100.324	0.4857	0.0472	1.00074	1.33311	0.1233	12.69
0.9171	100.66	0.9110	0.0888	1.0041	1.33370	0.1227	12.62[1]
1.1254	100.828	1.1162	0.1090	1.0058	1.33402	0.1235	12.71[1]
2.0110	101.48	1.9817	0.1949	1.0123	1.33522	0.1262	12.98[1]
2.1383	101.607	2.1044	0.2072	1.01354	1.33535	0.1234	12.70[1]
2.8718	102.186	2.8104	0.2784	1.01931	1.33639	0.1226	12.61[1]
2.9840	102.23	2.9218	0.2895	1.0198	1.33649	0.1246	12.82
4.6970	103.133	4.5543	0.4570	1.03268	1.33883	0.1255	12.91
2.3960	51.815	4.6241	0.4642	1.03320	1.33890	0.1254	12.90
3.4325	52.62	6.5288	0.6655	1.0490	1.34159	0.1241	12.77
3.8110	52.89	7.2055	0.7382	1.0544	1.34257	0.1247	12.83
3.9149	52.954	7.3936	0.7587	1.05600	1.34291	0.1252	12.88
4.7177	53.572	8.8063	0.9142	1.06832	1.34501	0.1244	12.80
		17.261	1.920	1.14479	1.35822	0.1245	12.81[2]
		46.06	6.716	1.5005	1.41841	0.1237	12.73[2]

TABLE VI.—POTASSIUM BROMIDE.

M = 119.02.

ws.	*wl.*	*p.*	*m.*	*d.*	*n.*	*k.*	M*k.*
3.7914	1001.45	0.3786	0.0318	0.99971	1.33292	0.1277	15.22
4.9685	503.18	0.9874	0.0832	1.00396	1.33370	0.1277	15.22
7.2169	504.80	1.4297	0.1210	1.00718	1.33408	0.1237	14.73
1.5140	101.079	0.4978	0.1268	1.00776	1.33425	0.1259	14.99[1]
2.9991	102.135	2.9364	0.2512	1.01829	1.33596	0.1247	14.84
3.7684	102.705	3.6692	0.3155	1.02373	1.33684	0.1251	14.89
4.2634	103.013	4.1387	0.3572	1.02704	1.33743	0.1260	15.00[1]
4.3275	102.635	4.2164	0.3640	1.02770	1.33749	0.1251	14.89
4.4345	103.131	4.2999	0.3714	1.02821	1.33763	0.1261	15.01
4.5802	102.809	4.4552	0.3852	1.02941	1.33777	0.1254	14.92[1]
7.5466	105.346	7.1636	0.6318	1.05006	1.34115	0.1254	14.92
8.3119	105.405	7.8856	0.6990	1.05543	1.34200	0.1255	14.94[1]
9.4012	106.178	8.8542	0.7907	1.06317	1.34327	0.1254	14.92
5.2158	53.645	9.7228	0.8736	1.06977	1.34435	0.1253	14.92
5.8142	54.098	10.7475	0.9799	1.07881	1.34575	0.1247	14.84
9.4922	45.164	21.017	2.061	1.16718	1.35984	0.1251	14.89

TABLE VII.—LITHIUM IODIDE.

M = 133.86.

ws.	*wl.*	*p.*	*m.*	*d.*	*n.*	*k.*	M*k.*
1.1125	100.377	1.1083	0.0832	1.33424	1.00509	0.1463	19.59
1.4318	100.610	1.4231	0.1070	1.33468	1.00742	0.1433	19.18
1.4602	100.623	1.4512	0.1092	1.33473	1.00755	0.1445	19.35
2.1668	101.149	2.1422	0.1621	1.33580	1.01282	0.1422	19.04
2.3885	101.305	2.3577	0.1785	1.33620	1.01438	0.1441	19.29
2.5650	101.434	2.5287	0.1917	1.33641	1.01567	0.1426	19.09
1.9882	40.013	4.9689	0.3838	1.34033	1.03405	0.1432	19.17
5.2155	42.367	12.3103	1.067	1.35311	1.09490	0.1417	18.97
6.7241	43.451	15.4751	1.298	1.35908	1.12291	0.1419	18.99

[1] Diluted from a more concentrated solution.

[2] Analyzed by precipitation of the bromine as silver bromide.

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TABLE VIII.—SODIUM IODIDE.

M = 149.92.

ws.	*wl.*	*p.*	*m.*	*n.*	*d.*	*k.*	Mk.
5.7423	1003.29	0.5723	0.0382	1.33333	1.00154	0.1289	19.32[1]
7.1559	1004.33	0.7125	0.0476	1.33352	1.00258	0.1291	19.36
7.1678	1004.36	0.7137	0.0477	1.33353	1.00261	0.1289	19.32
7.5042	1004.70	0.7469	0.0499	1.33362	1.00294	0.1299	19.47
3.8022	102.454	3.7111	0.2540	1.33793	1.02588	0.1302	19.52
3.9599	102.581	3.8603	0.2645	1.33817	1.02716	0.1300	19.49
7.1698	105.014	6.8272	0.4789	1.34278	1.05152	0.1300	19.48
8.2630	44.812	18.4384	1.425	1.36281	1.15808	0.1295	19.42
15.2028	49.977	30.418	2.621	1.38783	1.29156	0.1292	19.36

TABLE IX.—POTASSIUM IODIDE.

M = 166.02.

ws.	*wl.*	*p.*	*m.*	*d.*	*n.*	*k.*	Mk.
4.3878	1002.10	0.4379	0.0264	1.33306	1.00045	0.1263	20.97
9.2024	1005.58	0.9151	0.0553	1.33367	1.00382	0.1274	21.15
12.3546	1007.77	1.2259	0.0742	1.33409	1.00601	0.1299	21.57
2.3910	101.286	2.3607	0.1442	1.33554	1.01419	0.1304	21.64
3.1698	101.852	3.1122	0.1912	1.33658	1.01986	0.1305	21.67
5.2754	103.379	5.1029	0.3181	1.33927	1.03515	0.1295	21.50
9.1138	106.142	8.5864	0.5497	1.34422	1.06282	0.1295	21.50
12.0873	47.209	25.604	1.881	1.37194	1.2200	0.1289	21.40

From the data recorded in the foregoing tables various values of interest may be computed.

The increase in density of the solutions with increasing concentration is nearly, but not quite, proportional to the quantity of salt in unit volume. In Table X are given the quotients of the differences between the densities of the solution and of water divided by the molal concentrations:

TABLE X.

m.	LiCl.	NaCl.	KCl.	LiBr.	NaBr.	KBr.	LiI.	NaI.	KI.
0.05				0.060	0.078	0.083		0.117	0.123
0.10		0.0414		0.061	0.079	0.083	0.0964		
0.15	0.0246		0.047	0.0625		0.0843	0.0972		0.1187
0.2	0.0242	0.0405		0.0624	0.0787	0.0845	0.0970		0.1191
0.3	0.0240		0.0460		0.0790	0.0841	0.0964	0.1136	0.1196
0.5				0.0620	0.0779	0.0840		0.1137	0.1196
0.8	0.0242		0.0467	0.0622	0.0778	0.0834			
1.0		0.0399	0.0456		0.0780	0.0834	0.0972		
1.3	0.0236		0.0453				0.0969		
1.5	0.0235							0.1130	
1.8									0.1185
2.0			0.0448	0.0615	0.0769	0.0826			
2.5	0.0232	0.0386	0.0444	0.0611				0.1123	
3.5	0.0229		0.0441						
4.8				0.0604					
6.7					0.0750				

[1] Diluted from a more concentrated solution.

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These increments decrease slowly with increasing concentration except in the case of lithium iodide. Hence the curves on page 917 representing change in index of refraction with changing concentration are slightly convex with respect to the vertical axis. Furthermore, even at 2 molal concentration, where dissociation has taken place to the extent of about sixty per cent., the values in Table X show distinct additive relationships between the different salts. At lower concentrations

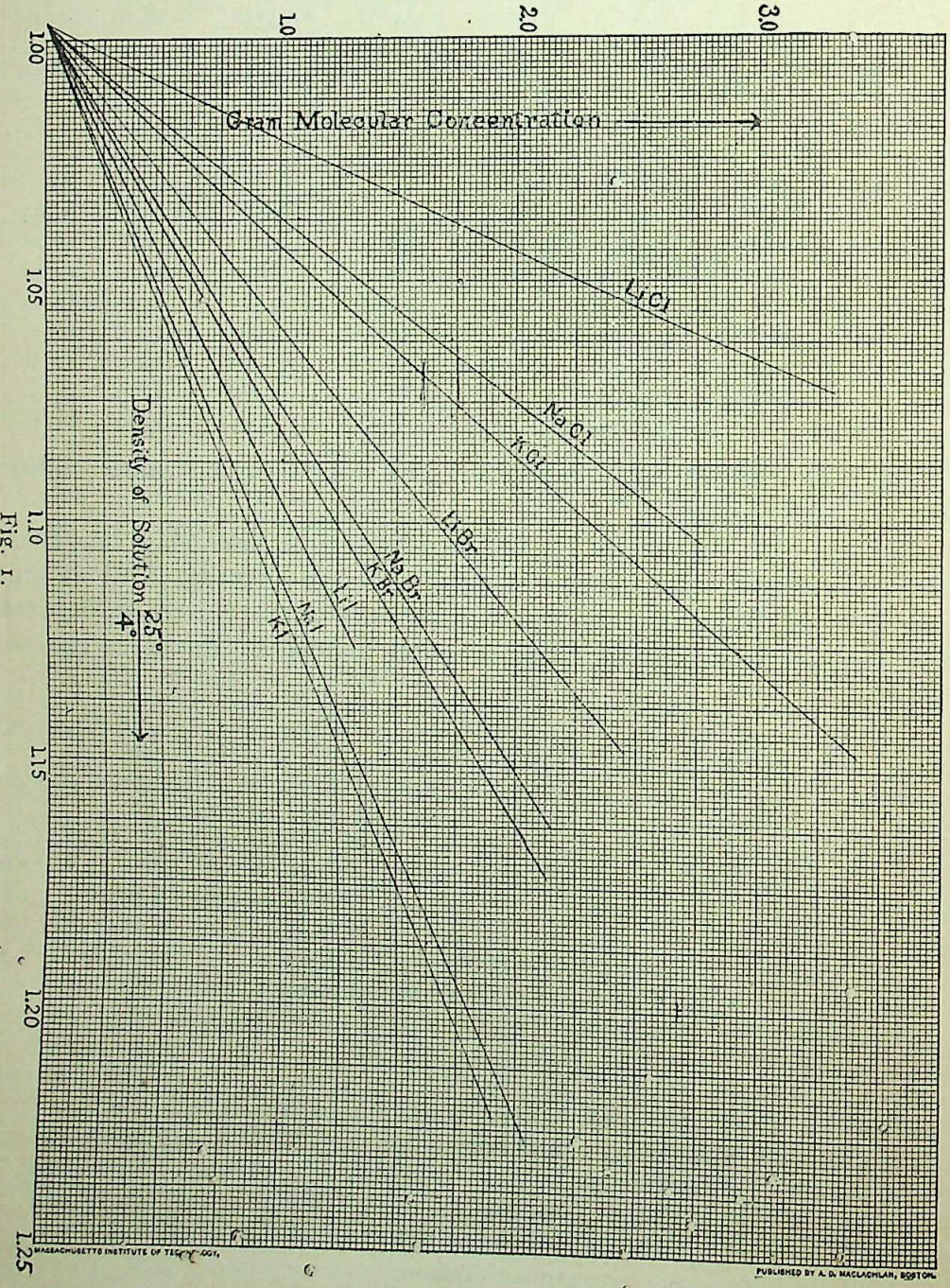


Fig. 1.

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the additive relations are still more striking, *i. e.*, for a given ion the increment is constant, although the effect of the molecules is evidently not far from additive. In Table XI are given the increments for the

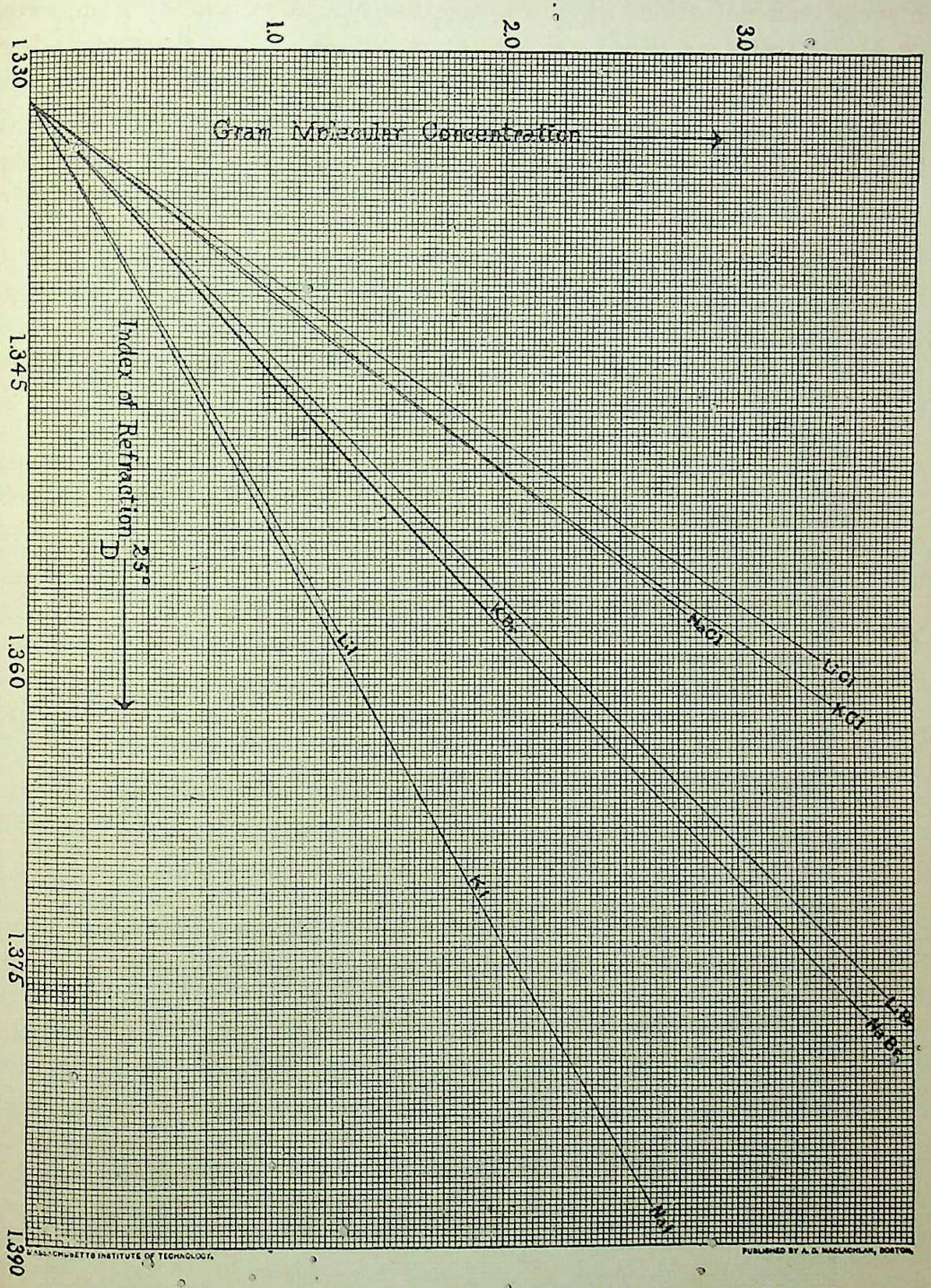


Fig. 2.

different salts in 1 molal solution, the values being taken from curves plotted with the results in Table X. It is to be noted that the differences as well as the increments change with the concentration:

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TABLE XI.

	Cl	Dif.	Br.	Dif.	I.
Li.....	0.0237	0.0382	0.0619	0.0351	0.0970
Dif.....	0.0162		0.0157		0.0163
Na.....	0.0399	0.0377	0.0776	0.0357	0.1133
Dif.....	0.0056		0.0057		0.0057
K.....	0.0455	0.0378	0.0833	0.0357	0.1190

These additive relationships were first pointed out by Valson[1] and have been frequently investigated by others. The calculations have been made here because the solutions were prepared at a somewhat higher

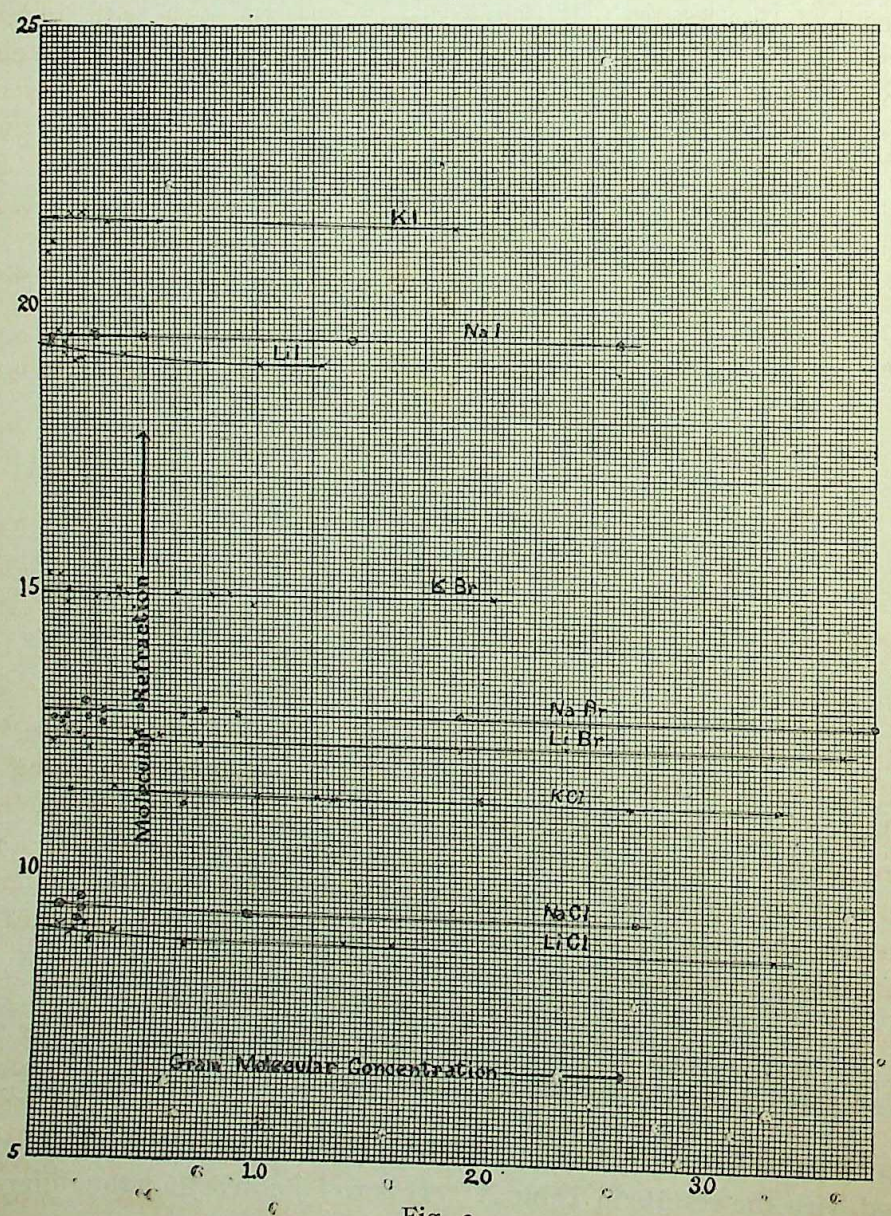


Fig. 3.

[1] *Compt. rend.*, 73, 441 (1871).

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temperature than has been commonly employed and because of the care with which the solutions were made up.

The cause of the decrease in the increments with increasing concentration is the increasing contraction which takes place during the solution of most salts in water, lithium bromide and iodide being exceptions to this rule and showing expansion during solution. This question of contraction and expansion during the solution of the alkali halides is discussed in a following paper.

In Table XII are given similar increments for change in the refractive index, obtained by dividing the differences between the refractive indices of the solution and of water by the molal concentration. As in the case of the density increments these values decrease with increasing concentration, although more slowly than the latter. Hence the curves on page 917 are slightly convex with respect to the vertical axis:

TABLE XII.

m.	LiCl.	NaCl.	KCl.	LiBr.	NaBr.	KBr.	LiI.	NaI.	KI.
0.05				0.0125	0.0134	0.0138		0.0222	0.0217
0.10		0.0102		0.0129	0.0138	0.0140	0.0208		
0.15	0.0095		0.0101	0.0131		0.0140	0.0205		0.0212
0.2	0.0091	0.0100		0.0129	0.0139	0.01385	0.02066		0.02144
0.3	0.0092		0.00997		0.0140	0.01380	0.02046	0.02148	0.02133
0.5	0.00892			0.01292	0.01380	0.01372		0.02150	0.02136
0.8			0.00973	0.01279	0.01370	0.01361			
1.0		0.00971	0.00965		0.01370	0.01354	0.02049		
1.3	0.00874		0.00949				0.02049		
1.5	0.00873							0.02129	
1.8									0.02098
2.0			0.00935	0.01256	0.01340	0.01327			
2.5	0.00850	0.00924	0.00910	0.01254				0.02111	
3.5	0.00838		0.00896						
4.8				0.01231					
6.7					0.01280				

As has already been pointed out by Bender and others, these increments exhibit additive relationships, which are more striking at low than at high concentrations, indicating that the ionic but not the molecular increments are nearly constant. Values, taken from curves, for 1 molal solutions are given in the following table. Here also the differences between the increments for corresponding salts are not constant with changing concentration:

TABLE XIII.

	Cl.	Dif.	Br.	Dif.	I.
Li.....	0.00885	0.00390	0.01275	0.00774	0.02049
Dif.....	0.00086		0.00090		0.00088
Na.....	0.00971	0.00394	0.01365	0.00772	0.02137
Dif.....	0.00006		0.00011		0.00017
K.....	0.00965	0.00389	0.01354	0.00766	0.02120

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The most noticeable feature of these results is the fact that the increments for potassium salts are uniformly lower than those for sodium salts, although lithium salts give the smallest increments. This peculiarity is undoubtedly closely connected with the contraction which takes place during the solution of the sodium and potassium salts, the contraction per gram molecule being *greater* with sodium than with potassium salts except with the iodides where the reverse is true. Lithium salts show smaller contractions than either sodium or potassium salts, the bromide and iodide in fact showing expansion during solution.

The specific and hence the molecular refractions of the different salts (see Tables I to IX) are nearly constant with varying concentration, although a very slight gradual increase in these constants with diminishing concentration is noticeable in all cases. In the case of lithium chloride and iodide this increase seems to be somewhat more marked at low concentrations. So marked an increase at so low concentration could hardly be due to increased dissociation in the case of electrolytes of so large a tendency to dissociate. Furthermore, if due to this cause, it is to be expected with all the salts examined. If caused by an unusually high degree of hydration, a similar effect is to be expected with lithium bromide where no such effect apparently exists. It is to be remembered that with the more dilute solutions the refractive constants are obtained by difference between two relatively large quantities, and consequently are less to be relied upon than the values obtained from the more concentrated solutions. Hence it is not at all impossible that the larger increase in the case of lithium chloride and iodide is due merely to experimental irregularities.

In comparing the molecular refractions of the different salts, in order to avoid as far as possible the effect of different degrees of dissociation, hydration or any other influences, it is well to select values for molecular refraction at equivalent concentrations, since then the above effects may be expected to be as nearly as possible the same in all cases. In the following table are given values taken from the curves of molecular refraction given on page 918, at unimolecular concentration:

TABLE XIV.

	Cl.	Dif.	Br.	Dif.	I.	Av.
Li.....	8.75	3.54	12.29	6.71	19.00	
Dif.....	0.50		0.51		0.43	0.48
Na.....	9.25	3.55	12.80	6.63	19.43	
Dif.....	2.10		2.11		2.05	2.09
K.....	11.35	3.56	14.91	6.57	21.48	
Av.....		3.55		6.64		

The additive relationships indicated by this table are as regular as could be reasonably expected.

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Obviously the foregoing table affords no means of determining directly the atomic refractions of the six elements involved. However, it is possible to obtain a value for the atomic refraction of hydrogen from measurements of the index of refraction and density of this substance in the gaseous state, the index of refraction of the gas for sodium light being 1.000138 referred to vacuum at 0° and 760 mm., and the density 0.0000896 under the same conditions.[1] The atomic refraction of hydrogen found in this way is 1.03. It may be added that Conrady[2] found the average atomic refraction of hydrogen in organic substances to be 1.05, a value in close agreement with the above. Although there is no positive evidence that the atomic refraction of hydrogen in the ionic state is identical with that of the gas or of the element in organic combinations, on account of the low value of this constant the error caused by such an assumption is probably small.

The molecular refraction of hydrochloric acid has recently been found in this laboratory[3] to be 8.53 at unimolal concentration at 25°. The difference between the value for hydrochloric acid and that for hydrogen, 7.50, may be assumed to represent the atomic refraction of chlorine. From the latter value the following tables of atomic refractions may be constructed:

TABLE XV.

H	=	1.03
Cl	=	7.50
Br	=	7.50 + 3.55 = 11.05
I	=	11.05 + 6.63 = 17.68
Li	=	1.25, 1.24, 1.32. Av. 1.27
Na	=	1.75, 1.75, 1.75. Av. 1.75
K	=	3.85, 3.86, 3.80. Av. 3.84

The values for chlorine, bromine and iodine are all considerably higher than the values for the same elements computed by Conrady[4] from results with organic compounds, 6.00, 8.93 and 14.12, respectively, while the indices of refraction and densities of chlorine and bromine gases yield the values 5.78 and 8.45.

It is evident from this table that the atomic refractions of the alkali metals in solution are relatively much smaller than those of the halogens, as was to be expected from an examination of the curves showing change in index of refraction with changing concentration. Furthermore, in the two series of similar elements, as Gladstone and Kanonnikoff have already pointed out, atomic refraction increases with increasing atomic weight. No further generalizations can safely be made from so limited a number of atomic refractions.

[1] Landolt-Börnstein-Meyerhoffer.

[2] *Z. physik. Chem.*, 3, 210 (1889).

[3] This investigation, by Mr. Frederick Barry, is not yet published.

[4] *Loc. cit.*

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The chief results of this research may be summed up as follows:

1. The densities and indices of refraction at 25° of solutions of the chlorides, bromides and iodides of lithium, sodium and potassium have been accurately determined at various concentrations.

2. The increments of density and refractive index for solutions of the above salts are calculated at 25° and are found to decrease slowly with increasing concentration and to be very closely additive at equivalent concentrations, especially at low concentrations.

3. It is pointed out that no refractive constant for one component of a solution, which is calculated upon the assumption that the specific refraction of the other component remains constant in solution and equal to that of the pure substance, is entirely satisfactory, since in general specific refraction, no matter by what formula calculated, changes with even slight changes in conditions.

4. The specific refractions of the salts in question, calculated by the Lorentz and Lorenz formula upon the assumption that the specific refraction of water does not change in solution, are found to be very nearly constant, but to increase very slightly with increasing dilution.

5. The molecular refractions of the nine salts are found to be very nearly additive at all concentrations.

The data given in this paper allow the computation of the change in volume during solution in water of the salts. This question is discussed in detail in the following paper.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

CHANGES IN VOLUME UPON SOLUTION IN WATER OF THE HALOGEN SALTS OF THE ALKALIS.

BY GREGORY PAUL BAXTER.

Received April 13, 1911.

It is commonly stated that when salts are dissolved in water the volume of the solution is less than the sum of the volumes of the salt and the water.[1] In some cases the volume of the solution is even less than the volume of the water alone.[2] Furthermore, the contraction is greater the more dilute the solution,[3] as is evident from the well known fact that usually contraction continues to take place as a solution is diluted. It is less well recognized that in a few instances the volume of the solution is greater than the sum of the volumes of the salt and the water,

[1] Nernst, *Theoret. Chem.*, trans., p. 381 (1904); Ostwald, *Lehrbuch*, 1, 782 (1903)

[2] Thomsen, *Therm. Untersuch.*, 1, 45 (1882). MacGregor, *Trans. Roy. Soc. Can.* 1890, 19; 1891, 15. *Trans. Nova Scotia Inst. Nat. Sci.*, 7, 368 (1890). Traube, *Z. anorg. Chem.*, 3, 1 (1892).

[3] Nernst, *Loc. cit.*

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although as early as 1873 Favre and Valson pointed out that this is the case with the halogen salts of ammonium.[1] Later Traube[2] showed that expansion takes place with lithium bromide and ammonium nitrate, although not with ammonium iodide. Quite recently, a similar expansion has been observed by Buchanan,[3] who found that in the saturated solutions of the halogen salts of cesium the "molecular volumes" of the salts in solution are greater than those of the solid salts, although the reverse is true with the corresponding salts of potassium and rubidium. Buchanan pointed out that this peculiarity indicates *contraction during crystallization.*

Previous attempts to correlate the sum of the volumes of the salt and the water and the volume of the resulting solution have been somewhat hampered by lack of sufficiently accurate density determinations, both with regard to the salts and their solutions, the chief error in the case of the solutions being due to inaccurate determination of concentration. The data furnished in the preceding paper[4] upon the refractive power of the halogen salts of lithium, sodium, and potassium in aqueous solution, together with recent specific gravity determinations of solids (see Table IV), allow the calculation of the change in volume during the solution of the foregoing salts with considerable certainty, and since these values were determined under essentially the same conditions they are strictly comparable. The interesting feature of the results is that not only the expansion during solution in the case of lithium bromide is confirmed, but also that lithium iodide is found to behave similarly.

In the following tables are given the data illustrating the magnitude of the changes in volume during solution for the fifteen salts of all the alkali metals with the halogens. The values in Table I, for the lithium, sodium, and potassium salts, are taken from the preceding paper. In the case of the rubidium and cesium salts Buchanan's results are employed, and for sake of comparison his experiments with potassium salts are given in Table II. The specific gravities of the solid salts used in the calculations are given in Table IV, except that in Buchanan's experiments his own values for the specific gravities are used. Buchanan's results for the specific gravities of the salts under consideration are probably slightly too low, owing to occlusion of mother liquor by the crystals used in the determinations, although the small differences between his values and those given in Table IV may be due in part, at least, to the fact that the data in Table IV refer to the fused salts:

[1] *Compt. rend.*, 77, 802 (1873).

[2] *Loc. cit.*

[3] *Am. J. Sci.*, 21, 25 (1906).

[4] Baxter, Boylston, Mueller, Black and Goode.

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TABLE I.

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water. cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
LiCl...	0.15	250.61	249.94	0.76	—0.09	—0.06	—2.5
	0.17	250.865	250.136	0.848	—0.119	—0.068	—2.9
	0.22	250.865	249.852	1.134	—0.121	—0.052	—2.2
	0.23	250.61	249.54	1.16	—0.09	—0.04	—1.7
	0.23	250.61	249.47	1.18	—0.04	—0.02	—0.8
	0.33	250.865	249.320	1.721	—0.176	—0.0494	—2.09
	0.66	100.405	99.195	1.360	—0.150	—0.0534	—2.26
	0.66	250.865	247.838	3.405	—0.378	—0.0537	—2.28
	1.39	100.432	97.766	2.868	—0.202	—0.0341	—1.45
	1.61	100.432	97.360	3.315	—0.248	—0.0355	—1.51
	2.64	100.432	95.316	5.441	—0.325	—0.0289	—1.23
	3.31	100.432	93.909	6.831	—0.308	—0.0218	—0.93
NaCl...	0.09	1001.75	1000.18	2.47	—0.90	—0.170	—9.9
	0.09	1001.75	1000.15	2.57	—0.98	—0.178	—10.4
	0.17	1001.75	998.77	4.69	—1.71	—0.170	—9.9
	0.18	99.869	99.526	0.499	—0.156	—0.146	—8.5
	0.19	501.20	499.49	2.60	—0.89	—0.160	—9.4
	0.95	99.869	98.103	2.547	—0.821	—0.1481	—8.66
	0.96	99.869	98.086	2.615	—0.832	—0.1488	—8.70
	2.70	38.695	36.610	2.856	—0.771	—0.1262	—7.38
KCl....	0.13	1001.75	998.20	4.77	—1.22	—0.128	—9.6
	0.13	100.45	100.08	0.49	—0.12	—0.12	—9.0
	0.13	250.57	249.65	1.23	—0.31	—0.126	—9.4
	0.13	501.20	499.33	2.52	—0.65	—0.129	—9.6
	0.13	250.57	249.67	1.26	—0.36	—0.143	—10.7
	0.33	100.45	99.50	1.24	—0.29	—0.117	—8.7
	0.33	100.45	99.49	1.26	—0.30	—0.118	—8.8
	0.64	501.20	492.03	11.99	—2.82	—0.118	—8.8
	0.67	100.45	98.62	2.50	—0.67	—0.134	—10.0
	0.67	100.45	98.57	2.50	—0.62	—0.124	—9.3
	0.67	100.45	98.58	2.50	—0.63	—0.126	—9.4
	1.00	100.45	97.54	3.76	—0.85	—0.113	—8.3
	1.00	100.45	97.54	3.77	—0.86	—0.114	—8.4
	1.28	100.45	96.79	4.79	—1.13	—0.118	—8.8
	1.34	100.45	96.53	5.01	—1.09	—0.109	—8.1
	1.35	99.869	95.927	5.032	—1.090	—0.109	—8.1
	2.00	100.45	94.41	7.53	—1.49	—0.099	—7.4
	2.01	100.45	94.47	7.53	—1.55	—0.103	—7.7
	2.67	100.45	92.32	10.03	—1.90	—0.0950	—7.08
	2.68	100.45	92.31	10.06	—1.92	—0.0958	—7.14
	3.30	100.45	90.33	12.38	—2.26	—0.0925	—6.80
	3.34	100.45	90.16	12.54	—2.25	—0.0900	—6.71
LiBr...	0.02	100.25	100.18	0.06	+0.01	+0.05	+4.0
	0.04	100.25	100.16	0.10	—0.01	—0.03	—3.0
	0.05	100.25	100.14	0.11	0.00	0.00	0.0

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TABLE I (*continued*).

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water. cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
LiCl....	0.05	100.25	100.12	0.12	+0.01	+0.02	+2.0
	0.09	100.25	100.00	0.24	+0.01	+0.01	+1.0
	0.12	100.25	99.95	0.30	0.00	0.00	0.0
	0.17	99.869	99.460	0.414	—0.005	—0.003	—0.3
	0.20	100.25	99.76	0.49	0.00	0.00	0.0
	0.22	50.17	49.91	0.27	—0.01	—0.01	—1.0
	0.42	50.17	49.65	0.53	—0.01	—0.006	—0.5
	0.42	50.17	49.65	0.53	+0.01	+0.006	+0.5
	0.44	50.17	49.61	0.56	0.00	—0.00	0.0
	0.51	50.17	49.54	0.64	—0.01	—0.005	—0.4
	0.55	50.17	49.48	0.69	0.00	0.000	0.0
	0.74	50.150	49.228	0.936	—0.014	—0.0043	—0.43
	1.92	50.20	47.75	2.42	+0.03	+0.004	+0.3
	2.39	50.15	47.048	3.011	+0.091	+0.0087	+0.76
	4.83	27.167	23.687	3.290	+0.190	+0.0168	+1.46
NaBr...	0.05	100.250	100.130	0.162	—0.042	—0.086	—8.8
	0.09	100.25	100.03	0.30	—0.08	—0.09	—9.0
	0.11	100.250	99.995	0.373	—0.118	—0.104	—10.7
	0.19	100.25	99.76	0.67	—0.18	—0.09	—9.0
	0.21	100.250	99.760	0.709	—0.219	—0.102	—10.5
	0.28	100.250	99.605	0.953	—0.308	—0.107	—11.0
	0.29	100.25	99.68	0.99	—0.28	—0.094	—9.7
	0.46	99.869	98.723	1.558	—0.412	—0.088	—9.1
	0.46	50.150	49.564	0.795	—0.209	—0.088	—9.1
	0.67	50.16	49.33	1.14	—0.31	—0.090	—9.3
	0.74	50.16	49.22	1.26	—0.32	—0.084	—8.6
	0.76	50.146	49.183	1.299	—0.336	—0.0860	—8.85
	0.91	50.146	48.998	1.565	—0.417	—0.0886	—9.12
	1.92	87.35	82.98	5.73	—1.36	—0.0788	—8.11
	6.71	66.64	54.10	15.30	—2.76	—0.0600	—6.18
KBr....	0.03	1001.75	1000.59	1.38	—0.22	—0.058	—6.9
	0.08	501.20	499.67	1.81	—0.28	—0.056	—6.7
	0.12	501.20	499.03	2.63	—0.46	—0.064	—7.6
	0.13	100.301	99.858	0.553	—0.110	—0.073	—8.7
	0.25	100.301	99.427	1.094	—0.220	—0.073	—8.7
	0.32	100.324	99.228	1.375	—0.279	—0.074	—8.8
	0.36	100.301	99.040	1.556	—0.295	—0.069	—8.2
	0.36	99.869	98.596	1.580	—0.307	—0.071	—8.5
	0.37	100.301	98.986	1.618	—0.303	—0.068	—8.1
	0.39	99.869	98.515	1.672	—0.318	—0.069	—8.2
	0.63	100.324	98.086	2.754	—0.516	—0.068	—8.1
	0.70	99.869	97.375	3.034	—0.540	—0.0649	—7.74
	0.79	99.869	97.061	3.431	—0.623	—0.0663	—7.90
	0.87	50.146	48.571	1.903	—0.328	—0.0629	—7.49
	0.98	50.146	48.426	2.122	—0.402	—0.0680	—8.10
	2.06	38.695	35.776	3.464	—0.545	—0.0574	—6.84

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TABLE I (*continued*).

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water. cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
LiI.....	0.08	99.869	99.556	0.274	+0.039	+0.035	+4.7
	0.11	99.869	99.468	0.353	+0.048	+0.034	+4.6
	0.11	99.869	99.454	0.360	+0.054	+0.037	+5.0
	0.16	99.869	99.272	0.534	+0.063	+0.0290	+3.9
	0.18	99.869	99.207	0.588	+0.074	+0.0309	+4.1
	0.19	99.869	99.155	0.632	+0.082	+0.0319	+4.3
	0.38	38.695	38.137	0.490	+0.068	+0.0342	+4.6
	1.01	38.695	37.260	1.284	+0.151	+0.0290	+3.88
	1.30	38.695	36.835	1.656	+0.204	+0.0307	+4.11
NaI....	0.04	1001.75	1000.48	1.57	—0.30	—0.052	—7.8
	0.05	1001.75	1000.10	1.95	—0.30	—0.042	—6.3
	0.05	1001.75	1000.12	1.96	—0.33	—0.046	—6.9
	0.05	1001.75	1000.13	2.05	—0.43	—0.057	—8.6
	0.25	99.869	98.942	1.038	—0.111	—0.0292	—4.38
	0.26	99.869	98.911	1.072	—0.114	—0.0288	—4.32
	0.48	99.869	98.131	1.956	—0.218	—0.0308	—4.62
	1.42	38.695	36.656	2.255	—0.216	—0.0262	—3.96
	2.62	38.695	34.876	4.148	—0.329	—0.0216	—3.24
KI.....	0.03	1001.75	1000.64	1.41	—0.30	—0.068	—11.3
	0.06	1001.75	999.31	2.95	—0.51	—0.055	—9.1
	0.07	1001.75	998.35	3.97	—0.57	—0.046	—7.6
	0.14	99.869	99.186	0.768	—0.085	—0.036	—6.0
	0.19	99.869	98.972	1.018	—0.121	—0.0382	—6.34
	0.32	99.869	98.392	1.694	—0.217	—0.0414	—6.88
	0.55	99.869	97.313	2.926	—0.370	—0.0406	—6.74
	1.88	38.695	35.225	3.880	—0.410	—0.0339	—5.63

TABLE II.

Salt.	Gram molecular concentration.	Volume of solution. cc.	Volume of water.[1] cc.	Volume of salt. cc.	Change in volume during solution. cc.	Change in volume per gram of salt. cc.	Change in volume per gram molecule of salt. cc.
KCl.....	4.14	1148.5	1000.0	182.1	—33.6	—0.0947	—7.06
KBr.....	4.67	1223.5	1000.0	254.5	—31.0	—0.0455	—5.41
KI.....	6.19	1442.3	1000.0	487.7	—45.4	—0.0306	—5.07
RbCl.....	6.00	1295.7	1000.0	347.3	—51.6	—0.0549	—6.65
RbBr.....	5.18	1296.7	1000.0	346.6	—49.9	—0.0449	—7.43
RbI.....	5.55	1482.1	1000.0	510.2	—28.1	—0.0161	—3.42
CsCl.....	7.62	1595.9	1000.0	514.4	+81.5	+0.0398	+6.70
CsBr.....	4.22	1255.4	1000.0	253.7	+ 1.7	+0.0015	+0.32
CsI.....	2.86	1240.9	1000.0	204.5	+36.4	+0.0395	+10.25

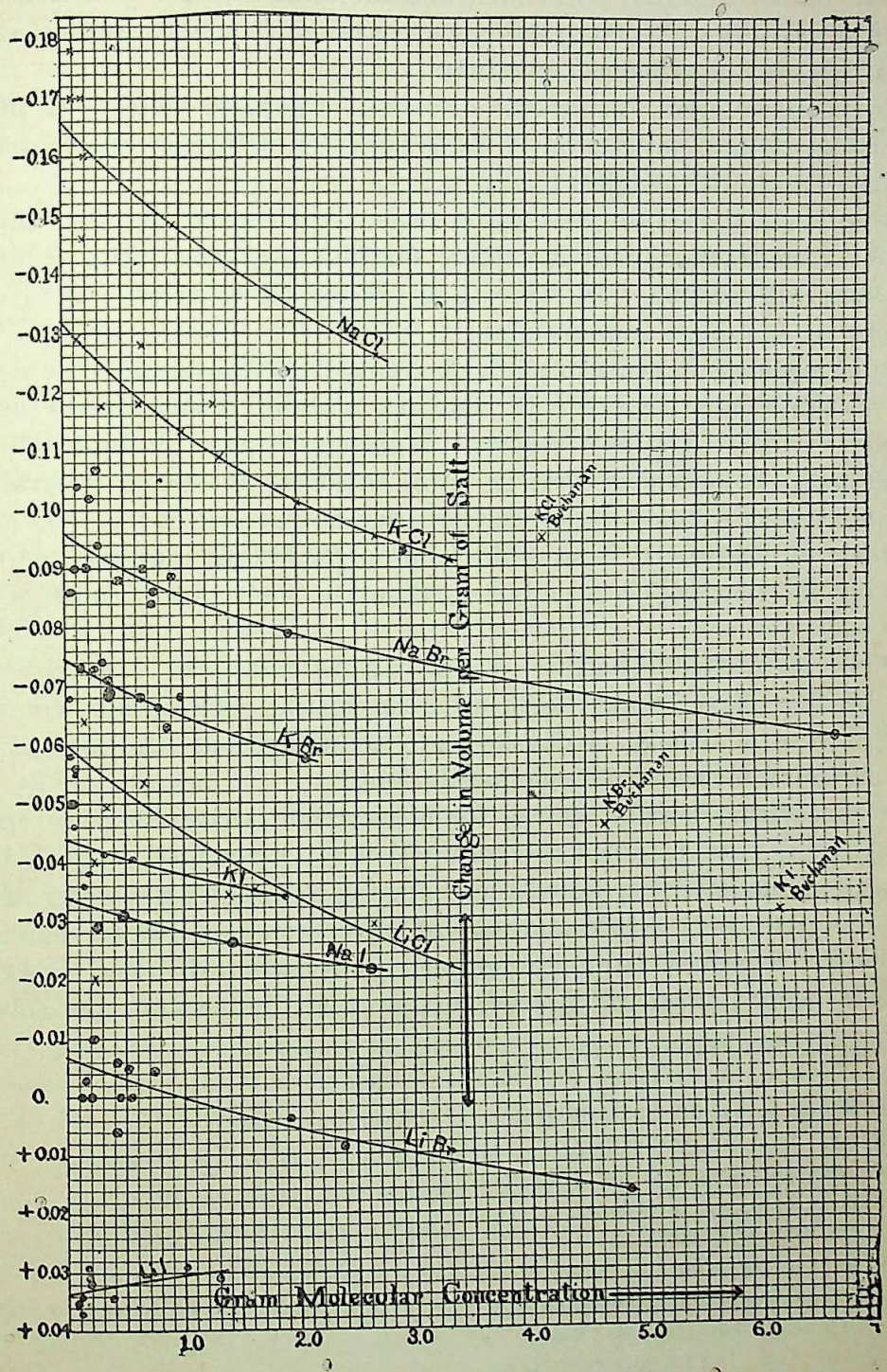
As has already been pointed out, the chief feature of interest in the foregoing tables is the fact that in the case of five of the salts the volume

[1] For convenience, Buchanan's results are referred to 1000 cc. of water, although the experiments were carried out with much smaller quantities.

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of the solution is greater than the sum of the volumes of the water and the salt, *i. e.*, that *expansion* takes place during solution. It is noticeable



that such cases are confined to the salts of lithium and cesium, lithium chloride being the only halogen salt of either of these metals which shows contraction upon solution, and even with this salt the contraction per

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gram molecule is considerably less than in the case of any one of the nine other salts which exhibit contraction.

With salts of sodium, potassium, and rubidium and the same halogen, in all three series the contraction per gram molecule varies somewhat irregularly within rather narrow limits.

On the other hand, in the case of salts of the same metal with different halogens, the contraction is always greater with chlorides and with bromides than with iodides.

From inspection of the curves on page 927 it can be seen that the increase in contraction with increasing dilution is greatest with chlorides and least with iodides. In the case of lithium iodide there is increasing *expansion* with dilution if anything.

Many attempts have been made to connect mathematically the densities of solutions with the salt content. Valson,[1] Favre and Valson,[2] Nicol,[3] Bender,[4] Traube,[2] Rogow,[5] Kohlrausch and Hallwachs,[6] and Kohlrausch[7] have shown that in dilute solutions of strong electrolytes the increase in volume of the solvent, due to the solution of one gram molecule of electrolyte, is an additive property, which increases with increasing dilution and is usually less than the molecular volume of the solid salt.

The researches of Charpy,[8] Wade,[9] Barnes and Scott,[10] Forch[11] and Heydweiller[12] have brought forth other interesting relationships concerning the rate of change in density with changing concentration as well as concerning molecular volume in solution.

In considering possible causes for contraction during solution many investigators have assumed the contraction to be confined to the solute, although some have attributed the change in volume to the water alone. In a few cases both solute and solvent have been assumed to change in volume.[13] The first two assumptions are purely arbitrary, however, no facts being known which tend to show that both solute and solvent

[1] *Compt. rend.*, 73, 441 (1871).
[2] *Loc. cit.*
[3] *Phil. Mag.*, [5] 16, 121 (1883).
[4] *Wied. Ann.*, 20, 560 (1883).
[5] *Z. physik. Chem.*, 11, 657 (1893).
[6] *Wied. Ann.*, 53, 14 (1894).
[7] *Ibid.*, 56, 185 (1895).
[8] *Compt. rend.*, 109, 299 (1899).
[9] *J. Chem. Soc.*, 75, 254 (1899).
[10] *J. Physic. Chem.*, 2, 536 (1899).
[11] *Wied. Ann.*, [4] 12, 591 (1903).
[12] *Verh. d. d. physik. Ges.*, 11, 37 (1909); *Z. physik. Chem.*, 70, 128 (1910).
[13] Favre and Valson, Kohlrausch, Forch, *Loc. cit.* Ostwald, *Lehrbuch*, 1, 784 (1903). Tammann, "Ueber die Beziehung zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907, p. 78.

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do not participate in the change in volume. There can be no doubt that the water takes part in the change, since the solution in some cases occupies less volume than the water alone.

Tammann has discussed in detail the properties of solutions with reference to those of the solvent and has assumed, since solutions when subjected to changes of pressure and temperature behave approximately in the same way as the same volume of water at a higher pressure, a compression of the water by the solute owing to increase of internal pressure, termed "binnendruck." It is a matter of considerable uncertainty whether the compression of the water is applied to all the water or to only a portion. Either assumption is capable of explaining the observed regularities. Drude and Nernst's[1] hypothesis of "electrostriction" of the water in the field of the ions is no more specific in its nature. Furthermore, the compression of the salt itself is a factor which cannot be neglected and in the following pages the attempt is made to show that change in volume of the salt probably plays a considerable part in the final result.

Recent investigations by T. W. Richards[2] upon the significance of changing atomic volume as applied to a hypothesis of compressible atoms furnishes a basis for a possible explanation of changes in volume upon solution. This hypothesis involves the assumption of elastic atoms relatively large with reference to the "free space" and, in combination at least, probably in intimate contact. According to the hypothesis the elastic atoms are susceptible to both distortion and compression under the influence of chemical affinity, molecular (or atomic) cohesion, or external pressure.

In the first paper on the subject the following statement occurs apropos of the molecular volumes of hydroxides:[3]

"It is interesting to note that in this table, where the substances are arranged in the order of the contraction which ensues when hydroxyl combines with the metal, they *should also be arranged in the electrochemical order*. That is to say, the solution tension of a metal appears to be associated with the excess of affinity of the metal for hydroxyl over its affinity for itself, and intensity of potential seems to be associated with intensity of atomic compression. The inference to be drawn from this comparison is, of course, that the formation of the metallic ion in water is connected with the affinity of the metal for water—an affinity which manifests itself even when both the 'bonds' of oxygen are filled. Similar attraction for nitrogen or sulphur would explain cases in which the solvent does not contain oxygen.

[1] *Z. physik. Chem.*, 15, 79 (1894).
[2] *Proc. Am. Acad.*, 37, 3 (1901); 37, 399 (1902); 38, 293 (1902); 39, 581 (1904).
[3] *Ibid.*, 37, 12.

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"If this is true, contraction should take place when salts are dissolved in water. This inference is amply verified by facts. In some cases the solution occupies even less space than the water alone, involving a total contraction greater than the volume of the salt itself. The best known of these cases are those of lithic, sodic and baric hydroxides, and cobalt, nickel, zinc and magnesium sulphates, but undoubtedly others exist. In a large majority of cases when an electrolyte is dissolved in water, the sum of the volumes of the salt and of the solvent taken together considerably exceeds the volume of the solution. This contraction is usually ascribed wholly to the dissolved substance in dilute solutions, but it seems to me that the behavior of the salts named above proves the falsity of this method of calculation. *The water as well as the salt must contract when a salt is dissolved.* So many complications are concerned in the act of the solution of an electrolyte that it is difficult to unravel the tangled clues; but the wide deviations exhibited by different substances seem to indicate that there are present overlapping contractions and expansions, the resultant of which is a smaller quantity than some of the individual influences. Such contractions and expansions are just what one would expect to find in a readjustment of affinities."

It is evident from the fact that the solution of salts in water may be accompanied by either an increase or a decrease in volume that at *least two important influences must be at work, one involving expansion, the other contraction.* Experimentally it is possible to observe only the resultant of the combined effects. Although on this account it is difficult to discover the nature and the magnitude of the individual influences, the foregoing hypothesis of compressible atoms suggests the following possible causes of change in volume during solution in the case of electrolytes dissolving in water.

(1) If, when the salt dissolves, partial dissociation takes place, this initial disintegration of the molecule is undoubtedly accompanied by change in volume, since it is well known that the molecular volume of a salt is not equal to the sum of the atomic volumes of its constituents. Richards has pointed out that in the case of the halogen salts of lithium, sodium, and potassium the diminution in volume upon the union of the metal and the halogen is very considerable and is a function of the compressibilities of the free elements and of their affinities for each other.[1] These data are given in Tables III and IV, certain slight changes having been made in Richards' table, owing to the availability of more reliable experimental work. There are added similar data for rubidium and cesium.

[1] *Proc. Am. Acad.*, 39, 585 (1904).

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TABLE III.

Element.	Atomic weight. Ag = 107.88.	Specific gravity.[1]	Atomic volume. cc.	Compressibility[2] megabars × 10⁶.	Heat of oxidation. Kilogram calories.	Heat of combination with hydrogen.[4] Kilogram calories.
Li.....	6.94	0.534	13.1	8.8	143 ($2M + O$)[3]	
Na.....	23.00	0.971	23.7	15.4	101 "	
K.....	39.10	0.862	45.4	31.5	87 "	
Rb.....	85.45	1.532	55.8	40.0	84 "	
Cs.....	132.81	1.87	71.0	61.0	83 "	
Cl.....	35.46	1.412	25.0	95.0	—18 (Cl_2O)	22.0
Br.....	79.92	3.121	25.6	51.8		8.4
I.....	126.92	4.94	25.7	13.0	45 (I_2O_5)	—6.0

TABLE IV.

Salt.	Molecular weight.	Specific gravity[5] of fused salt.	Sum of atomic volumes. cc.	Molecular volume. cc.	Contraction in formation of solid = a. cc.	Change in volume[6] during solution = b. cc.	$a + b$. cc.	Compressibility[7] megabars × 10⁶.
LiCl.....	42.40	2.07	38.1	20.5	—17.6	— 1.91	—19.5	
LiBr.....	86.86	3.46	38.7	25.2	—13.5	+0.03	—13.5	
LiI.....	133.86	4.06	38.8	33.0	— 5.8	+4.02	— 1.8	
NaCl.....	58.46	2.14	48.7	27.2	—21.5	— 8.64	—30.1	4.1
NaBr.....	102.92	3.08	49.3	34.2	—15.1	— 8.85	—24.0	5.1
NaI.....	149.92	3.67	49.4	40.9	— 8.5	— 4.26	—12.8	6.9
KCl.....	74.56	2.00	70.4	37.3	—33.1	— 8.47	—41.6	5.0
KBr.....	119.02	2.74	71.0	43.5	—27.5	— 7.72	—35.2	6.2
KI.....	166.02	3.12	71.1	53.4	—17.7	— 6.28	—24.0	8.6
RbCl.....	120.91	2.75	80.8	44.0	—36.8	— 6.65	—43.5	
RbBr	165.37	3.28	81.4	50.5	—30.9	— 7.45	—38.4	
RbI.....	212.37	3.44	81.5	61.9	—19.6	— 3.40	—23.0	
CsCl.....	168.27	3.97	96.0	42.4	—53.6	+ 6.74	—46.9	
CsBr.....	212.73	4.38	96.6	48.6	—48.0	+ 0.43	—47.6	
CsI.....	259.73	4.51	96.7	57.7	—39.0	+10.4	—28.6	

During solution the portion of the salt which is dissociated is freed not only from the compression due to chemical affinity but also from that due to molecular cohesion, for in the solution the ionic cohesion

[1] For the specific gravities of the alkali metals see Richards and Brink, THIS JOURNAL, 29, 117 (1907).

[2] Richards, Stull and Bonnet, *Pub. Car. Inst.*, 76, 15 (1907); Richards and Stull, *Ibid.*, 7 (1904).

[3] Abegg, *Handb. d. anorg. Chem.*, Vol. II, Part I.

[4] Landolt-Börnstein-Meyerhoffer, *Tabellen.*

[5] For the specific gravities of the iodides and the rubidium and cesium salts, see Archibald, *J. Chem. Soc.*, 85, 776 (1904); Richards and Archibald, *Proc. Am. Acad.*, 38, 453 and 465 (1903); Baxter and Brink, THIS JOURNAL, 30, 46 (1907).

[6] The values for the first nine salts refer to molal solutions and are obtained by multiplying values taken from the curves on page 927 by the molecular weight. The values for the rubidium and cesium salts refer to the concentrations of Buchanan's experiments.

[7] Richards and Jones, THIS JOURNAL, 31, 158 (1909).

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must be negligible in comparison with that between the particles of solid or liquid elements. Furthermore, in the case of the halogens at any rate the self-affinity is considerable, as is shown by the diatomic molecules, and in the ionic form the halogen is probably free from the compression due to this self-affinity. Hence the contraction during the formation of the solid salt from the elements is even less than the expansion to be expected upon dissociation.

The fact that *expansion during solution of solids in water is known to occur only with strong electrolytes* supports the idea that in the dissociation of the molecules the atoms are freed from the compression due to chemical combination.

This cause of increase in volume is not the only one which may be suggested. As Richards has pointed out,[1] the charged ions may be subjected to more or less distension through electrical self-repulsion. Furthermore, even in the case of the undissociated portion of the salt slight expansion during solution probably occurs, since the substance is freed at least from the compression due to molecular cohesion. Both of these effects are probably much less important than the one outlined above.

That this expansion during dissociation is far from being the most important factor which influences change in volume during solution is evident from the fact that sodium, potassium, and rubidium salts, as well as lithium chloride, exhibit *contraction* during solution, while in the case of only one of the other five salts, lithium iodide, does the expansion during solution approach the value of the contraction in the formation of the solid salt from its constituent elements (columns 6 and 7, Table IV). It is to be noted that the values for the change in volume during solution in the case of the lithium, sodium, and potassium salts refer to molal solutions in which the salts are about seventy-five per cent. dissociated. In the case of the rubidium and cesium salts the values refer to much more concentrated solutions and are undoubtedly smaller than for less concentrated solutions, at least for the salts which show contraction during solution.

(2) As opposing this tendency toward expansion during solution, it is natural to consider any tendency toward combination between the water and the salt, *i. e.*, either ionic or molecular hydration. While it is reasonable to suppose that hydration in general increases with increasing dilution and diminishes with rising temperature, knowledge of the exact extent of this hydration is at present very limited.[2] The most reliable quantitative measurements of ionic hydration are those by Washburn,[3] who has determined the relation of the average hydration of the

[1] *Proc. Am. Acad.*, 37, 16 (1901).

[2] For a critical review of the subject of hydration see Washburn, *Technology Quarterly*, 21, 360 (1908).

[3] THIS JOURNAL, 31, 322 (1909).

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lithium, sodium and potassium ions to that of the chlorine ion in 1.2 molal solution to be 4.7, 2.0 and 1.3, respectively, at 25°. From the work of Biltz, H. C. Jones, and others, it is probable, however, that the hydration of the cesium ion is the least of those of the alkalies, and that the chlorine ion is more and the iodine ion less hydrated than the bromine ion.

With regard to the hydration of molecules, evidence is still less certain, especially with electrolytes. The possession of crystal water may be considered evidence of the presence of hydrated molecules in solution, and roughly a measure of the extent of the hydration. On the other hand, the absence of crystal water does not preclude the existence of hydrated molecules in solution. In the case of the fifteen salts under consideration, only lithium and sodium salts crystallize with water of crystallization at ordinary temperatures. Judging from the number of molecules of water of crystallization and the stability of the solid hydrates, one might conclude that the hydrates of molecular lithium halides in solution contain more combined water and are more stable than those of sodium, and those of sodium more than those of the other alkali metals. Further generalizations are evidently unwarranted.

The effect of the hydration of the ions upon the total volume of the products will obviously depend not only upon the extent of the hydration and the affinity of the elements for the water, but also upon the compressibility of the metal or halogen on the one hand and that of water on the other. Since the compressibility of water is relatively large, 48 x 10^{-6} megabars, its compression by combination in hydration is undoubtedly an important factor in changes in volume in aqueous solutions. With regard to the compressibility of water, Richards[1] has already pointed out that there is good reason for believing that in the water molecule the hydrogen is much more compressible than the oxygen. Hence, with an element which has a strong affinity for oxygen a smaller compression of the water is to be expected than with an element of strong affinity for hydrogen.[2]

An approximate idea of the relative affinities of the different elements under consideration for oxygen and hydrogen may be obtained by comparing the heats of combination of the elements with oxygen and hydrogen, as given in Table III. In the case of the metals the affinity for oxygen is greatest with lithium, varying only slightly with the other four elements. The compounds of these metals with hydrogen are so unstable that their affinities for hydrogen must be negligible. In the case of the halogens the affinity for oxygen is much lower than in the case of the metals, and is considerably less with chlorine than with iodine. This is

[1] *Proc. Am. Acad.*, 39, 593 (1904).

[2] This suggestion was made to me by Prof. Richards.

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in accordance with the relative affinities of the halogens for hydrogen, the relation being the reverse of those with reference to oxygen. Thus in general, since the compression by the metallic ion is probably applied to the less compressible oxygen, one might expect *the compression of the water through hydration of the metallic ions to be much less than through the hydration of the halogen ions.* In the case of the halogens *the compression of the water through the hydration of the chlorine ion should be most and through that of the iodine ion least.*

In the case of strong electrolytes the effect of the hydration of molecules in producing change in volume during solution is undoubtedly smaller than that of the hydration of ions. In the first place, even in a four times molal solution nearly fifty per cent. of an alkali halide is dissociated. In the second place, the salts themselves are much less compressible than the elements (see Tables III and IV), so that *the change in volume due to hydration of the molecules may be attributed chiefly to the compression of the water.*

Thus it appears that the opposing tendencies towards expansion and contraction during solution are greater with ions than with molecules, *i. e.*, that *the ions are responsible for the greater part of the changes in volume which take place during solution.*

In connection with the foregoing explanation of change in volume during solution the following statement by Favre and Valson is of interest:

"Lorsq'un sel se dissout, on peut admettre qu'il se produit deux effets de sens inverse, (1) un effet de contraction du dissolvant sous l'influence du sel, (2) un effet d'augmentation de volume du sel, par suite de la dissociation plus ou moins avancée de ses elements constituants. Le premier effet est, dans le généralité des cas, plus considerable que le second, de sorte que le résultat final est ordinairement une contraction."

Upon the assumption that the change in volume upon solution in water of one of the salts in question is chiefly due to the *difference* between the expansion due to dissociation and the contraction due to hydration, it is a difficult matter in any particular case to predict whether the resultant will be a negative or positive quantity. One might expect, however, that the observed contraction or expansion would not be very large in any case. This is in fact true.

In comparing the salts of the different metals we find that the contractions during the formation of the solid salts from the elements show a very considerable continuous increase from lithium to cesium in the five sets of metallic salts, the difference between rubidium and cesium salts being especially large. It is probable, then, that corresponding expansions take place during dissociation.

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Although the metallic ions differ considerably in the extent to which they are hydrated, since, as has been already pointed out, the effect of the metallic ions in compressing the water molecules is probably applied chiefly to the oxygen which is the less compressible portion of the water, only slight differences among the metallic ions are to be expected as far as the compression of the water is concerned. The compressibilities of the different metals are undoubtedly of far greater importance than the extent of the hydration or the affinities for oxygen in determining the contraction due to hydration. These compressibilities increase rather rapidly with increasing atomic volume, lithium being a very slightly compressible substance, but cesium being seven times as compressible. Thus the greater hydration of the lithium ion is compensated by its lesser compressibility, while the lesser hydration of the cesium ion is compensated by its greater compressibility.

It is not at all surprizing, therefore, to find the lithium and cesium salts exhibiting either expansion during solution or very slight contraction, the lithium salts chiefly because of the small compressibility of lithium, and the cesium salts because of the large contraction during the formation of the solid salts from the elements, and the small hydration.

With regard to the comparison of the chlorides, bromides, and iodides, the contraction during the formation of the solid salts is in every case greatest with chlorides and smallest with iodides. Although no certain evidence is available concerning the relative hydration of the halogen ions, it is highly probable that the chlorine ion is most and the iodine ion least hydrated. This, together with the high heat of combination of chlorine and hydrogen and the negative heat of combination of iodine with hydrogen, leads one to expect much greater compression of the hydrated water molecules in the case of chlorine than in the case of iodine, while the low compressibility of iodine would tend still farther to cause the contraction during the hydration of the iodine ion to be less than that of the other halogens. Bromine is intermediate in its properties between chlorine and iodine. Hence, in spite of the smaller contraction during the formation of the solid iodides, a smaller contraction or a larger expansion during solution of iodides than of chlorides may be reasonably expected, as is actually the case.

A still more rational comparison of the different salts is obtained by finding the algebraic sum of (*a*) the change in volume during the formation of the solid salt from the solid or liquid elements and (*b*) the change in volume during solution. This sum, which is indicated in the eighth column of Table IV, although it makes no allowance for incomplete dissociation, may be considered a measure of the *contraction produced in the formation of the ions from the free elements*. These figures do not

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refer to the same concentrations with the rubidium and cesium salts as with the others, still the values may be legitimately used for purposes of comparison.

The sum is the smallest in the case of the lithium salts and largest with cesium salts, while it is smallest with iodides and largest with chlorides, cesium chloride and bromide being only the exceptions. Even here the discrepancy is very small and easily accounted for by the high concentration at which the contraction during solution for cesium chloride was determined; that is, of the metals which have the greatest affinity for oxygen and least for hydrogen and which therefore can be expected to compress the water less than do the halogens, those with the smallest compressibility give the smallest values for this sum; while of the halogens, which have a relatively large affinity for hydrogen and which therefore may be expected to compress the water to a greater extent, chlorine, with the greatest affinity for hydrogen, the highest hydration, and the greatest compressibility gives the largest value for the sum of the contractions.

In the case of lithium iodide where the causes for contraction are least, the observed expansion during solution is nearly seventy per cent. of the contraction during the formation of the solid salt from the elements, a rather striking coincidence in connection with the fact that the salt at the concentration in question is between seventy and seventy-five per cent. dissociated. On the other hand, cesium chloride and bromide yield maximum values, as is to be expected.

If the sum, $a + b$, represents the contraction in the formation of the ions from the elements, it should be an additive property with different salts. Table V contains the values of this sum in cubic centimeters per gram molecule for the salts of lithium, sodium, and potassium at molal concentration, these salts all being very nearly seventy-five per cent. dissociated under these conditions. Table VI contains the corresponding values for zero concentration, obtained by prolonging the curves on page 927. Since the values in Table VI apply to complete dissociation they are of greater interest than those in Table V. The rubidium and cesium salts are not included because the single values for the change in volume during solution were obtained at different concentrations, all of which were much higher than molal:

TABLE V.

	Cl	Dif.	Br	Dif.	I
Li	19.5	6.0	13.5	11.7	1.8
Dif.	10.6		10.5		11.0
Na	30.1	6.1	24.0	11.2	12.8
Dif.	11.5		11.2		11.2
K	41.6	6.4	35.2	11.2	24.0

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TABLE VI.

	Cl	Dif.	Br	Dif.	I
Li	20.1	6.0	14.1	12.8	1.3
Dif.	11.1		10.9		12.3
Na	31.2	6.2	25.0	11.4	13.6
Dif.	11.7		11.4		11.3
K	42.9	6.5	36.4	11.5	24.9

In both tables the additive relations are as close as could be expected when the variety of data upon which the values depend is considered.

Obviously, the foregoing data do not afford a means of calculating the change in volume in the formation of any one ion from the free element. However, the lithium and iodine ions taken together show almost no change in volume in their formation from the free elements. It is possible that this result is due to partial compensation by *expansion* in the formation of one ion and *contraction* in the formation of the other. Of these two elements the lithium is the less compressible, but its ion is more hydrated than the iodine ion. Furthermore, lithium iodide contains eighteen times as much iodine as lithium by weight. All things considered, one cannot be far wrong in assuming that the change in volume is equally distributed between the lithium and iodine ions. Upon this basis the following table has been constructed to show the change in volume in the formation of six ions from the elements at infinit dilution. The values are expressed in cubic centimeters per gram atom:

TABLE VII.

Li	0.7	Cl	18.8
Na	12.1	Br	12.6
K	23.8	I	0.7

It is interesting to note, as Ostwald has already pointed out,[1] that the heat evolved in the formation of an ion from the free element is a constant. This fact is well illustrated by the additive relationships in the algebraic sum of the heat of formation and the heat of solution of salts. The two latter values for the lithium, sodium, and potassium halides are given in Table VIII, and the sums of the two in Table IX:

TABLE VIII.

Salt.	Heat of formation, kg. cal.	Heat of solution, kg. cal.
LiCl	93.8	+ 8.4
LiBr	80.0	+11.4
LiI	61.2	+14.9
NaCl	97.7	— 1.2
NaBr	85.7	— 0.2
NaI	69.1	+ 1.3
KCl	105.6	— 4.4
KBr	95.3	— 5.1
KI	80.1	— 5.1

[1] *Grundriss der Allgemeinen Chemie*, 280 (1899).

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TABLE IX.

	Cl	Dif.	Br	Dif.	I
Li	102.2	10.8	91.4	15.3	76.1
Dif.	5.7		5.9		5.7
Na	96.5	11.0	85.5	15.1	70.4
Dif.	4.7		4.7		4.6
K	101.2	11.0	90.2	15.2	75.0

(3) Blanchard[1] has called attention to the fact that, if, as is commonly believed, liquid water consists in part of polymerized molecules $(H_2O)_x$, the formation of hydrates in solution will alter the equilibrium between the simple molecules and the polymers. Since there is evidence that the change from the polymerized molecules to the simple molecules is accompanied by contraction, if in hydration the simple water molecules combine with the hydrated substance, so that a portion of the polymerized molecules dissociate into simple molecules, it is obvious that in this way also hydration would produce contraction during solution. On the other hand, if in hydration the polymerized molecules are ever combined with the hydrated substance, it is probable that such a change would produce expansion, owing to the formation of new polymers at the expense of the simple molecules.

It is not only uncertain to what extent these phenomena take place during the solution of a salt, but it is also uncertain to what extent water is polymerized at ordinary temperatures. The formation of the polymerized water molecules is certainly retarded by rising temperature. If the first assumption is correct, *i. e.*, if in hydration the simple water molecules combine with the hydrated ion, then the contraction during solution would be greatest with the ions which are most extensively hydrated. This is, however, not the case, for while the chloride ion produces more contraction than the less hydrated bromide ion, and the iodide ion, which is probably least hydrated, produces least contraction, the lithium ion, which is the most hydrated of all the metallic ions, produces far less contraction, than the sodium, potassium and rubidium ions, although slightly more than the cesium ion. The facts fit the case no better if the assumption is made that hydration is combination with polymerized water. Hence this factor, although it may be of influence, is undoubtedly of less importance than the two which have been discussed.

If the resultant effect of dissociation is to produce contraction, then, since dissociation and probably hydration increase with the dilution, the contraction per gram molecule of salt should increase with the dilution, as is the case with seven of the nine salts for which the change with the dilution was investigated. With lithium iodide, on the other hand,

[1] THIS JOURNAL, 26, 1318 (1904).

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the resultant is expansion, hence the expansion should increase with the dilution. This seems actually to be the case to a slight extent, although with lithium bromide, where the increase in volume is very slight at all concentrations, the reverse is apparently true. The latter fact may be due to the compensating effect of the increased hydration which accompanies dilution.

The formation of hydrates in aqueous solution is undoubtedly hindered by rising temperature, while the dissociation changes only slightly. Hence the contraction due to hydration would be less, while the expansion due to dissociation would remain nearly constant, since the temperature coefficient of expansion of solids is usually small. Consequently any resultant diminution in volume during solution ought to decrease with rising temperature, while a resultant increase in volume should still further increase. This is in accordance with the fact pointed out by Traube[1] that "molecular solution volume" increases with rising temperature to a maximum between 50° and 70°.

The foregoing explanation of the causes of changes in volume during solution is proposed as a tentative one, to be further tested and amplified. It is obvious that at present it would have been impossible, upon the basis of the known properties of the elements and compounds in question, to predict with certainty whether the resultant effect in any case would be expansion or contraction, although some idea might be obtained as to whether the resultant effect would be large or small. Undoubtedly other influences than those which have been proposed affect the changes in volume during solution. From so limited a range of material to arrive at a complete and accurate knowledge of the phenomena involved could hardly be expected, and no claim is made that such a result has been reached. The purpose of this paper is to call attention to the following facts which certainly cannot be disregarded in any consideration of the subject.

(1) No adequate explanation of the causes of the changes in volume which actually take place during the solution of electrolytes in water has been proposed.

(2) The existing data show beyond question that the phenomena which take place are complex. Since these phenomena include both contraction and expansion, at least two important influences must be at work.

(3) Upon the basis of Richards's hypothesis of compressible atoms and that of hydration, an explanation of the observed effects with the class of alkali halides has been devised. This explanation assumes that at any rate the following two changes take place during solution and dissociation:

[1] *Z. anorg. Chem.*, 8, 55 (1895).

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(*a*) The salt is freed in large part from compression due to chemical affinity and to molecular cohesion.

(*b*) When the ions and probably the molecules are combined with the water both the hydrated substance and the water undergo compression. This latter effect varies regularly with the compressibilities of the substances involved as well as with their affinities for each other.

(4) It is shown that the change in volume in the formation of the ions from the elements, as measured by the sum of the change in volume in the formation of the solid salt and the change in volume during solution, is an additive property.

(5) The part which the polymerization of water plays in the change is uncertain. Probably this effect varies in importance with varying temperature. It is also probable that at the temperature of the experiments cited, the effect is small, since the observed effects are not in accord with those to be expected if the contraction is due wholly to changing polymerization.

It is obvious that the data furnished at the beginning of this paper allow the calculation of the densities of aqueous solutions of many of the salts considered up to moderately high concentrations.

The study of change in volume during solution will be continued in this laboratory by the examination of other salts and other solvents, and by the determination of the effect of varying temperature on the magnitude of the observed effect.

CAMBRIDGE, MASS.

THE DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM.

BY JAMES M. BELL AND ALEXANDER L. FEILD.

Received April 22, 1911.

The distribution of ammonia between water and chloroform has been studied by several investigators. The results have been employed to determin the concentration of free ammonia in an aqueous solution, which contains also some compound of ammonia, such as the blue cuprammonia compounds and the phosphates of ammonium. Until recently the distribution was determined only for dilute solutions, where the concentration of ammonia in the water layer was not greater than normal.

Hantzsch and Sebaldt[1] found that the ratio of the concentrations of ammonia in water and chloroform is 25.1 at 25°, the mean of five determinations in which the concentration in the water layer varies from 0.00275 to 0.04425 normal. At 2° this ratio is 38.53. Dawson and McCrae[2] give the following values for the distribution ratio: 26.3 at 20°, 24.9 at

[1] *Z. physik. Chem.*, 30, 258 (1899).

[2] *J. Chem., Soc.*, 77, 1239 (1900).

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25°, and 23.2 at 30°, the highest concentration in the water layer being 14.14 grams NH_3 per liter. In a later paper Dawson and McCrae[1] repeated their determinations at 20°, the extreme concentrations of ammonia in the water layer being 5.160 and 17.168 grams NH_3 per liter. Between these limits the distribution ratio is not quite independent of the ammonia concentration. The ratio varies from 26.36 for the most dilute solution to 25.32 for the most concentrated.

The following quotation is from a later paper by Dawson:[2] "In reference to the distribution of ammonia between pure water and chloroform, it has already been shown that the concentration ratio H_{H_2O}/C_{CHCl_3} decreases with increasing ammonia concentration, but the relationship between these two factors could not be determined with a desirable degree of accuracy in the case of dilute solutions containing less than 0.5 mol. of ammonia per liter of aqueous solution." Consequently new determinations were made at 19.5° by an improved method. Representing k (the distribution ratio) as a function of c' (the concentration in the chloroform layer) the points so obtained lie approximately on the straight line corresponding to the equation

$$k = 26.16 - 34.14c'.$$

Abbott and Bray[3] have also found the distribution ratio with the object of determining the degree of hydrolysis of several phosphates of ammonium in aqueous solution. At 18° the ratio is 27.45, where the aqueous layer has a concentration between 0.02 and 0.05 normal.

In more concentrated ammonia solutions, Dawson[4] has found that at 18° the distribution ratio decreases from 26.46 at 0.928 normal to 21.70 at 4.333 normal.

The present paper contains the results of an investigation of this distribution at 25° and over a much wider range of concentration. Chloroform was added to aqueous solutions of ammonia of varying strength. The bottles were placed in an electrically heated and controlled thermostat at 25° and were frequently shaken. When equilibrium had been reached, a known volume of each layer was titrated against standard acid. The following table contains the concentration of ammonia in each layer expressed in gram molecules per liter and also the distribution ratio between the two layers.

It will be seen from the table that the distribution varies from 22 in dilute solution to about 10 in concentrated solution. The limit to which the distribution tends at very great dilution appears to be about 24

[1] *J. Chem. Soc.*, 79, 493 (1901).
[2] *Ibid.*, 99, 1668 (1906).
[3] This Journal, 31, 729 (1909).
[4] *Z. physik. Chem.*, 69, 110 (1909).

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TABLE I.

Normality NH_3 in water layer. C.	Normality NH_3 in $CHCl_3$ layer. C'.	Distribution ratio. K.
1.02	0.045	22.7
2.08	0.095	21.9
3.13	0.146	21.4
3.98	0.205	19.4
5.24	0.283	18.5
6.25	0.365	17.1
7.29	0.457	15.9
8.34	0.549	15.2
9.35	0.710	13.2
10.23	0.864	11.8
11.24	1.045	11.0
12.23	1.227	10.0

The following table contains the limiting values of the distribution ratio for very dilute solutions as found at different temperatures by the various workers in this field.

TABLE II.

Temp.	Dist. Ratio.	Observer.
2°	38.5	Hantzsch and Sebaldt.
18	27.45	Abbott and Bray.
18	27.5 approx.	Dawson.
20	26.5	Dawson and McCrea, I.
20	25.3	Dawson and McCrae, II.
25	25.1	Hantzsch and Sebaldt.
25	24.9	Dawson and McCrea, I.
25	24. approx.	Bell and Feild.
30	23.2	Dawson and McCrae, I.

The accompanying table (II) shows clearly that the distribution ratio falls as the temperature rises.

The points obtained by plotting the values of c and k in Table I lie on a curve which deviates rather far from a straight line, so that the formula given by Dawson holds only for the more dilute solutions, and is of value in giving the limiting direction of the curve. This result is confirmed by the later results of Dawson where more concentrated solutions have been used.

The effect of other compounds on the distribution ratio has been investigated by Hantzsch and Sebaldt[1] and by Dawson and McCrae.[2] As ammonia is a weak base it is but slightly ionized even at great dilutions, and consequently the addition of an ammonium salt would increase the number of undissociated molecules very slightly, while the percentage decrease of ionization would be greatly diminished. If unionized ammonia is the substance distributed, then the presence of ammonium chloride

[1] *Z. physik. Chem.*, **30**, 258 (1899).

[2] *J. Chem. Soc.*, **79**, 493 (1901).

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should affect the distribution very slightly and then only on account of the "salting out" effect. If, on the other hand, the ionized portion were distributed, the presence of the highly ionized salt would affect the distribution very greatly. In very dilute solutions Hantzsch and Sebaldt have found that ammonium chloride has almost no effect. Dawson and McCrae have, however, shown that the effect is measurable, the distribution ratio at 20° decreasing by 0.88 for each mol. of salt per liter of solution. The nitrate and sulfate also lower the distribution ratio, while the bromide increases it. The following table (III) gives the results of experiments on the distribution of ammonia between chloroform and a solution of ammonium chloride containing about 3 mols. per liter. At each concentration of ammonia the distribution ratio is very close to that found in the absence of ammonium chloride.

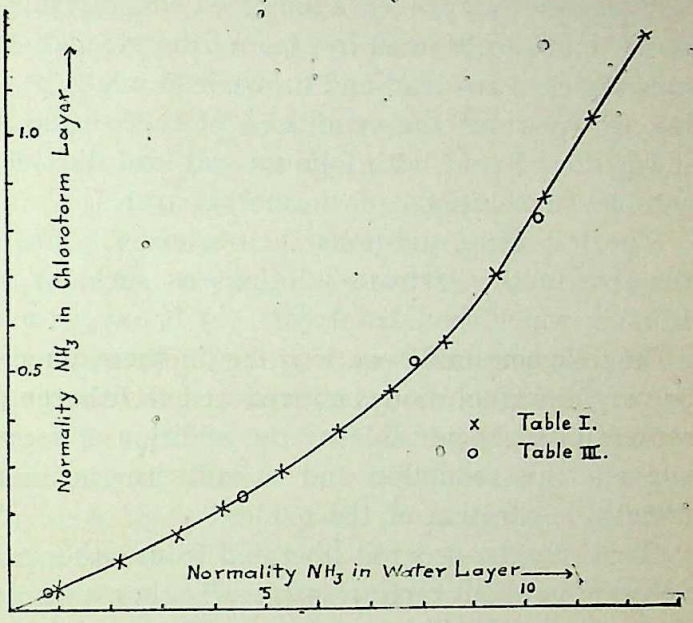


TABLE III.

Normality NH_3 in water layer (NH_4Cl—3N).	Normality NH_3 in $CHCl_3$ layer calc.	Normality NH_3 in $CHCl_3$ layer obs.
0.84	0.037	0.037
4.32	0.226	0.228
7.72	0.494	0.512
10.16	0.837	0.820

In this paper it has been shown that at 25° the distribution ratio for ammonia between water and chloroform varies with the concentration, from about 24 in dilute solution to about 10 in concentrated solution. The presence of ammonium chloride affects the distribution very slightly.

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ACTION OF THE OXIDES OF LEAD ON POTASSIUM TARTRATE.

BY FRANCIS C. KRAUSKOPF.

Received April 17, 1911.

The solvent action of solutions of normal alkali tartrates on litharge

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was discovered and studied in detail by Kahlenberg and Hillyer.[1] Later some of the physical properties of these double tartrate solutions were investigated by Kahlenberg.[2] This solubility of litharge in solutions of normal alkali tartrates and the apparent insolubility of red lead and brown lead in the same solvents indicated that by this means red lead or brown lead might be obtained free from litharge, and that the amount of litharge in samples of red lead and brown lead might be determined. In attempting to work out the conditions of these separations and determinations it was found that both minium and lead dioxide are after all appreciably soluble in solutions of normal tartrates.

The following questions then arose: (1) Do red lead and brown lead dissolve in the tartrate solutions as such, or are they first reduced to litharge which then dissolves? (2) Is oxygen evolved during the solution of the higher oxides of lead, or is there an oxidation of the tartrate? (3) If the higher oxides are reduced to litharge by oxidizing the tartrate, would it not be possible by the addition of some mild oxidizing agent to prevent this reduction and so still use the method above suggested to effect a separation of the oxides?

That oxygen was not liberated from either minium or lead dioxide on solution in alkali tartrate was easily shown by the following experiments: A gas buret, C (Fig. 1), was connected to a flask, B, by means of the condenser A. A solution of potassium tartrate was boiled in the flask for several hours with about 10 grams of red lead, and the whole apparatus was allowed to cool to the original temperature. About one-third of the red lead had dissolved and the residue had undergone no apparent change. When this residue was treated with dilute acid, no carbon dioxide was given off, indicating that none of the tartrate had been oxidized to carbonate. The water in the gas buret regained its original height when the apparatus cooled, showing that no oxygen had been evolved. A repetition of the experiment produced the same results. When lead dioxide was used in place of minium no evolution of oxygen could be

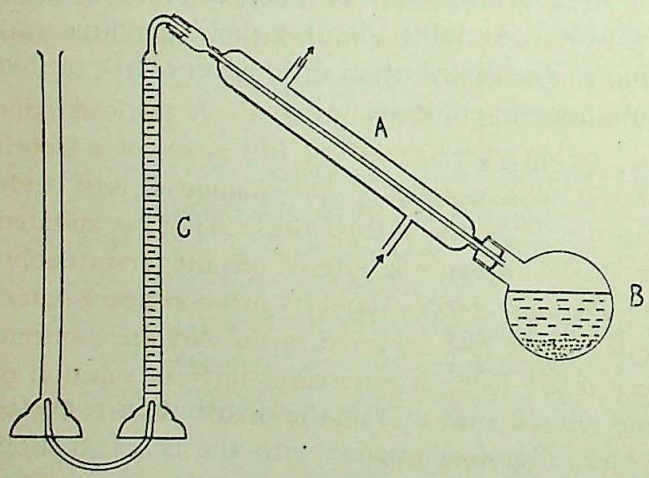


Fig. 1.

[1] *Am. Chem. J.*, 16, 94 (1894).

[2] *Z. physik. Chem.*, 17, 577 (1895).

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detected, but on continued boiling the residual lead dioxide was found to be mixed with a large amount of white residue. This residue gave off carbon dioxide readily when treated with dilute acid, which indicated an oxidation of the tartrate to carbonate.

When litharge dissolves in potassium tartrate it causes a certain definit change in the rotatory power of the tartrate solution, depending on the amount of lead oxide dissolved.[1] If red lead is first reduced to litharge which then dissolves the amount of change in rotation caused by any given amount of red lead should be the same as that caused by a chemically equivalent amount of litharge. If these changes in rotation were not the same, it would be still further proof that the red lead dissolves as red lead and that the potassium tartrate does not first reduce the red lead to litharge.

Four hundred grams of tartaric acid were just neutralized by potassium hydroxide and the solution made up to one liter. This solution in a 200 mm. tube had a rotation of $+35.76°$ at 20°. Minium does not dissolve as readily as litharge in the tartrate solution, and it is hard to get the last traces of a sample of minium to dissolve. Again, the amount of minium that dissolves in a given time varies with the amount of oxide in contact with the solution. Accordingly various amounts of minium were weighed out into 200 cc. flasks, and to each sample there was added 50 cc. of the tartrate solution. The flasks were closed with corks to prevent evaporation, and kept in a water bath at 50° for four days. The flasks were shaken frequently to hasten the solution.

At the end of this time the rotation of the solution above the lead oxide was determined. The lead oxide was filtered off by means of a Gooch crucible, washed, dried at 180° and weighed. The amount of lead oxide dissolved was thus determined. From the filtrate the lead was precipitated by means of hydrogen sulfide, the lead sulfide filtered off, the tartrate solution evaporated to its original bulk (50 cc.) and its rotation again determined in order to see if any change had occurred in the tartrate solution.

Similar experiments were made using a potassium tartrate solution of approximately one-half the concentration of the original. This solution had a rotation of $+17.60°$ in a 200 mm. tube.

The red lead used in the above experiments was from a Merck sample marked chemically pure. It was digested for a short time with dilute potassium tartrate solution to remove any small amounts of litharge, washed well and dried at 180° to constant weight. 1.8749 grams of this dried sample when ignited gave 1.8307 grams of litharge. According to theory it should give 1.8311 grams.

The litharge used was a chemically pure preparation of Merck's.

The following tables show the results of these experiments.

[1] *Z. physik. Chem.*, 17, 577 (1895).

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TABLE I.

Changes in rotation of a solution of normal potassium tartrate upon the addition of red lead and of litharge. Rotation of original tartrate solution + 35.76°.

		(A).			(A').		
No.	Pb_3O_4 in 50 cc. Grams.	Rotation.	Diminution of rotation.	Rotation with lead removed.	PbO in 50 cc. Grams.	Rotation.	Diminution of rotation.	Rotation with lead removed.	A—A'.
1	0.3606	35.05°	0.71°	35.61°	0.3576	35.32°	0.44°	35.69°	0.29°
2	0.5930	34.35	1.41	35.70	0.5791	34.90	0.86	35.72	0.61
3	0.6512	34.16	1.60	35.67	0.6361	34.76	1.00	35.70	0.60
4	0.8463	33.60	2.16	35.62	0.8267	34.41	1.35	35.68	0.81
5	1.2842	32.40	3.36	35.57	1.2546	34.36	1.40	35.75	1.96

TABLE II.

Same as Table I using a tartrate solution approximately half as concentrated, having a rotation of +17.60.

		(A).			(A').		
No.	Pb_3O_4 in 50 cc. Grams.	Rotation.	Diminution of rotation.	Rotation with lead removed.	PbO in 50 cc. Gram.	Rotation.	Diminution of rotation.	Rotation with lead removed.	A—A'
1	0.2486	16.84°	0.76°	17.55°	0.2427	16.98°	0.62°	17.56°	0.14°
2	0.3811	16.55	1.05	17.58	0.3730	16.73	0.87	17.56	0.18
3	0.4689	16.35	1.25	17.58	0.4580	16.61	0.99	17.59	0.26
4	0.5392	16.22	1.38	17.60	0.5265	16.49	1.11	17.58	0.27

From the above tables the following facts are evident: (1) The rotation of potassium tartrate solutions is diminished by the addition of either litharge or red lead. (2) This diminution increases as the concentration of the oxide in the solution increases. (3) In all cases when the lead is removed the rotation of the tartrate solution returns to practically its original value. (4) The diminution of rotation caused by any amount of minium is in all cases slightly greater than that caused by a chemically equivalent amount of litharge.

Summary.

The results of this investigation may be summarized as follows:

1. Because of the appreciable solubility of both minium and lead dioxide in solutions of normal potassium or sodium tartrate, it is impossible to determin the amount of litharge in a sample of either of these oxides by extraction with such solutions.

2. When minium or lead dioxide dissolves in potassium tartrate solution no evolution of oxygen occurs.

3. When lead dioxide dissolves in potassium tartrate solutions an oxidation of the tartrate occurs with concomitant precipitation of lead carbonate, while red lead dissolves without appreciable oxidation of the tartrate.

4. Red lead dissolved in normal potassium tartrate solution gives slightly greater diminution of the rotation than a chemically equivalent amount of litharge, indicating that red lead is not reduced to litharge before dissolving.

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To Professor Kahlenberg who suggested this work the author wishes to express thanks for kind and helpful criticism.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN,
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NOTES.

The Distribution of Hydrogen Sulfide in a Large Laboratory and the Use of Aluminium Stopcocks.—The problem of supplying hydrogen sulfide to a large number of students working in a chemical laboratory, when the work is being done at a number of points widely separated, is usually a more or less difficult one. Any ideas that will simplify this condition may be of interest to those in charge of large laboratories. The hydrogen sulfide system which was installed in the new chemical laboratory at the University of Michigan a little more than a year ago has been working so satisfactorily that a brief description of the essential features will be given.

The generators are placed in a small room located in the attic, so as to be above the level of all rooms in which hydrogen sulfide is used. The hydrogen sulfide generator room adjoins the attic storeroom which is reached by means of an elevator, so that supplies of ferrous sulfide and hydrochloric acid may be easily taken up. The hydrogen sulfide generator room is supplied with a small exhaust fan operated by an independent motor, and the waste pipe for carrying away the spent solution from the hydrogen sulfide generators connects directly with the main sewer outside the building. These two devices prevent the escape of gas into the attic or into the rest of the building through the water waste risers. There are two generators installed, one to supply the hydrogen sulfide, the other being held in reserve for use when it is necessary to clean or fill the first. The generators used are substantially like the one described by A. W. Browne and M. F. Mehling in THIS JOURNAL, 28, 838 (1906).

The main generating bottle has been modified by the addition of one tubular at the top and of one opposit the bottom tubular. The extra top tubular is closed with a solid rubber stopper and is used for introducing fresh ferrous sulfide without the necessity of disturbing the glass connections.

As the amount of work done in this laboratory calls for the use of 500 kilos of ferrous sulfide per year, it is necessary to add ferrous sulfide about once a week and hydrochloric acid almost daily. On account of the large amount of ferrous sulfide used, a certain amount of finely divided, insoluble material tends to accumulate in the bottom of the generator. By introducing a rapid stream of water through the bottom tubular opposit the spent acid discharge, any finely divided material can be flushed out and the ferrous sulfide kept clean and active.

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The hydrogen sulfide after leaving the generator is first passed through a water wash bottle and then through a tower of calcium chloride, before it enters the iron pipe distributing system. Two calcium chloride towers are installed. By means of two-way stopcocks either tower may be used for drying the gas while the calcium chloride in the other tower is emptied into a large evaporator, dried and regenerated for use. There is practically no loss of calcium chloride and a tower lasts from one to two weeks before it is necessary to empty and dry the calcium chloride.

The distribution of the dried hydrogen sulfide is effected by means of ordinary gas pipes. A $1^1/_4$-inch main connects with the generator. The $1^1/_4$-inch main extends across the building connecting at both ends with one-inch lines extending in the attic almost the length of the building on both sides. From various points in the one-inch distributing mains in the attic $^3/_4$-inch risers lead down to the rooms in which hydrogen sulfide may be desired. Two feet below the ceiling of each room through which a riser passes, a tee is placed, the tees being plugged in rooms where hydrogen sulfide is not being used at present. By this system hydrogen sulfide connections are provided for in eight rooms on the first floor, twelve on the second floor, twelve on the third, and sixteen on the fourth floor. Where hydrogen sulfide is used in a room, a one-half inch pipe connects the tee with a similar pipe running along the top of the hood in which the hydrogen sulfide is to be used. From the one-half inch pipe running along the top of the hood, $^3/_8$-inch pipes lead down to a convenient height for use. On the lower end of each $^3/_8$-inch pipe is screwed a special aluminum stopcock. These stopcocks were made in the University Shops. A mixture of equal parts of No. 1 aluminum and No. 12 casting alloy furnished by the Aluminum Company of America was used for casting the blanks from which the finished stopcocks were made. These stopcocks resemble in form an ordinary laboratory gas cock, except that the hole in the tip is made small to prevent excessive loss of gas if the cock is left open. We have used a hole 1 mm. in diameter, but this seems to be too large and 0.5 mm. would probably be better.

By having the generating system placed well above the level of the highest point at which the gas is used no trouble has been experienced in getting a satisfactory gas pressure at any point in the system, and as the aluminum stopcocks are not acted upon by dry hydrogen sulfide, these stopcocks, if occasionally lubricated, give no more trouble than ordinary gas cocks with illuminating gas.

E. D. CAMPBELL.

ANN ARBOR, MICH.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 190.]

RESEARCHES ON QUINAZOLINES (TWENTY-SEVENTH PAPER). THE SYNTHESIS OF 3-AMINOARYL-4-QUINAZOLONES FROM ACYLANTHRANILS AND AROMATIC DIAMINES.

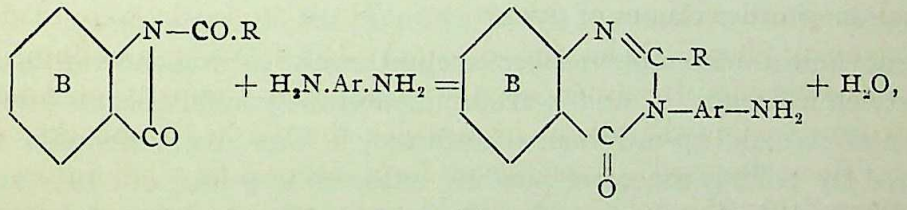
BY MARSTON TAYLOR BOGERT, ROSS AIKEN GORTNER AND CARL GUSTAVE AMEND.

Received March 11, 1911.

In continuation of our study of the synthesis of quinazolines from acylanthranils and primary amines[1] we have investigated also the behavior of the aromatic diamines with various acylanthranils, and the present paper records some of the results.

It has been shown by Klaber[2] that when acetanthranils condense with primary aliphatic diamines the reaction is a complicated one, resulting in the formation of at least three distinct products, but no appreciable amount of the aminoalkylquinazolone. We were, therefore, somewhat surprized to discover that when aromatic primary diamines are condensed with acylanthranils under proper conditions, not only is the reaction a remarkably smooth and simple one, but the desired aminoarylquinazolone is often produced in practically theoretical yield. The condensation can be effected either by gently fusing the two together (best), or by heating a mixture of the two in a suitable solvent.

The reaction by which these new bases are formed may be represented as follows:



in which B is a simple or substituted benzene nucleus, R a simple or substituted alphyl or aryl radical, and Ar a simple or substituted aromatic radical.

The condensation thus depends upon the presence of at least one primary amino group, while the other aromatic amino group may be primary, secondary or tertiary.

The ease and rapidity with which these new amine bases may be obtained in high yield and purity opens up a most extensive field and one into which we have as yet made but a few hasty trips.

The aminoarylquinazolones carrying a primary amino group show in general the following properties: They are crystallin or pulverulent

[1] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902); Bogert, *et al.*, THIS JOURNAL, 27, 649, 1305, 1327 (1905); 28, 94, 884, 1449 (1906); 29, 82, 517, 729 (1907); 30, 807 (1908); 31, 943, 1071 (1909); 32, 119, 1297, 1654 (1910).

[2] Dissert., Columbia University, 1907, pp. 34, *et seq.*

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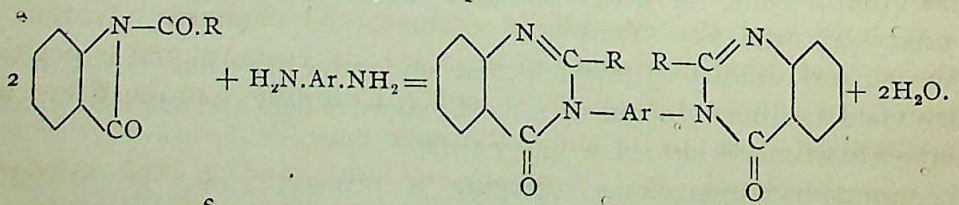
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solids of definit melting or decomposing points; very slightly soluble in water or in dilute aqueous solutions of the caustic alkalies; soluble in dilute hydrochloric or sulfuric acids, and more or less soluble in ninety-five per cent. alcohol. By careful purification, they can generally be obtained practically colorless, but on standing, or more rapidly on heating, they gradually darken.

When the primary amino groups are eliminated from these aminoarylquinazolones, the compounds thus obtained are not decomposed as to the nucleus when boiled with a twenty per cent. aqueous or alcoholic sodium hydroxide solution, but when fused with caustic alkali give aniline or substituted anilines. Many of these new bases are remarkably triboelectric. Diazotized in the usual way, they yield diazo or tetraazo salts which unite with suitable couplers to form valuable azo dyestuffs, some of which will be described in a subsequent paper.

The following diamines were used in our experiments: *o*-, *m*- and *p*-phenylenediamines, 2,4- and 2,5-diaminotoluene, benzidine, *o*-tolidine (3,3′-dimethyl-4,4′-diaminodiphenyl), ethoxybenzidine (3-ethoxy-4,4′-diaminodiphenyl) and dianisidine (3,3′-dimethoxy-4,4′-diaminodiphenyl). All of these condensed smoothly to aminoaryl quinazolones except the *o*-phenylene diamine. We have also condensed with acylanthranils di- and poly-amines containing but one primary amino group. The substances thus produced contain no diazotizable amino group, but can be used as couplers in the preparation of azo dyestuffs, or as starting points for the production of other classes of dyes.

The acylanthranils employed were acetanthranil,[1] 5-bromoacetanthranil,[2] 5-nitroacetanthranil,[3] 4- and 5-acetaminoacetanthranils,[4] benzoylanthranil,[5] and *m*- and *p*-nitrobenzoylanthranils. The acetanthranils were prepared by boiling the corresponding anthranilic acids, or their acetyl derivatives, with excess of acetic anhydride, while the benzoylanthranils were obtained by boiling the corresponding benzoylanthranilic acids with excess of acetic anhydride. The benzoylanthranils apparently do not yield aminoarylquinazolones under the same conditions as the acetanthranils, but rather diquinazolonyl compounds:



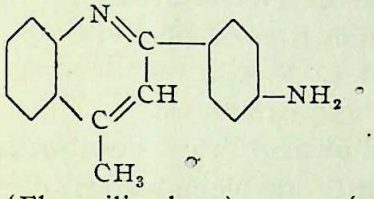
[1] Bogert and Seil, THIS JOURNAL, 29, 529 (1907).
[2] Bogert and Hand, *Ibid.*, 27, 1484 (1905).
[3] Bogert and Cook, *Ibid.*, 28, 1451 (1906).
[4] Bogert, Amend and Chambers, *Ibid.*, 32, 1297 (1910).
[5] Friedländer and Wleügel, *Ber.*, 16, 2229 (1883).

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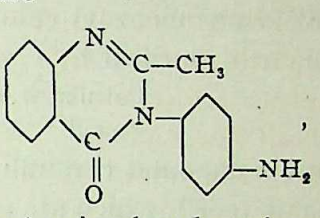
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Our experience has been to show that this diquinazolonyl formation occurs to a very limited extent, or not at all, with acetanthranil even when the latter is used in large excess. With the benzoylanthranils, however, as just stated, the chief product appears to be the diquinazolonyl, with little or no aminoarylquinazolone. Diquinazolonyls thus formed are readily isolated by virtue of their sparing solubility in the ordinary solvents.

A comparison of the formulas of these new amino compounds and flavaniline shows a rough similarity in structure



(Flavaniline base)



(2-Methyl-3-*p*-aminophenyl-4-quinazolone)

but on testing the above quinazolone compound, it was found when pure to be without tinctorial power.

Experimental.

I. Preparation of the Acylanthranils.

Acetanthranil is readily and rapidly prepared in large yield (80–90 per cent. of the theory) by the following simple process: Three parts of acetic anhydride are heated to 120–30° and one part finely pulverized anthranilic acid gradually added. The acetic acid formed as the by-product on the addition of the anthranilic acid immediately distils over (the temperature of the solution being kept above the boiling point of the acetic acid but below that of its anhydride), and the strength of the anhydride is thus maintained. After all the anthranilic acid has been added, the distillation is continued until the volume of the solution is reduced to about two-thirds or one-half its original bulk. On cooling, the acetanthranil generally crystallizes out at once. In case crystallization does not follow immediately upon cooling, it can be induced very easily by scratching the sides of the containing vessel or by seeding. In a properly arranged apparatus, the anthranilic acid can be added in a steady stream and (using 500 g. anthranilic acid) in 15–30 mins. the operation is usually completed and the crystallized acetanthranil obtained. As thus produced, and dried in absence of moisture, the acetanthranil is practically pure. In a moist atmosphere it rapidly hydrolyzes and must then be recrystallized from acetic anhydride once more.

5-Bromoacetanthranil,[1] *5-nitroacetanthranil*[2] and *4-* and *5-acetaminoacetanthranils*[3] were prepared as already described in the literature.

[1] Bogert and Hand, *Loc. cit.*
[2] Bogert and Cook, *Ibid.*
[3] Bogert, Amend and Chambers, *Ibid.*

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Benzoylanthranil[1] is easily obtained by boiling benzoylanthranilic acid with excess of acetic anhydride. It is not readily hydrolyzed by hot water, but boiling with dilute hydrochloric acid changes it to benzoylanthranilic acid. In the literature, the melting point of this anthranil is given as 122–3°. By recrystallization from acetic anhydride, we have raised its melting point to 124.5° (cor.).

m-Nitrobenzoylanthranilic acid, (1)HOOC.C_6H_4(2)NHCO$C_6H_4NO_2$ (*m*-).—An aqueous solution of sodium anthranilate was treated with the calculated amount of *m*-nitrobenzoyl chloride and the precipitated *m*-nitrobenzoylanthranilic acid purified by crystallization from alcohol.

Calculated for $C_{14}H_{10}O_5N_2$:	N, 9.79.
Found:	N, 9.84.

The pure compound crystallizes from alcohol in colorless prisms, melting at 233.5° (cor.), which are very slightly soluble in water.

p-Nitrobenzoylanthranilic acid, prepared in a similar manner from sodium anthranilate and *p*-nitrobenzoyl chloride, crystallizes from alcohol in small, nearly colorless needles, melting at 235.5° (cor.). It is more soluble in alcohol than the meta compound and explodes when heated suddenly.

Calculated for $C_{14}H_{10}O_5N_2$:	N, 9.79.
Found:	N, 9.80.

m-Nitrobenzoylanthranil, $\overline{CO.C_6H_4.NCOC_6H_4NO_2}$(*m*-), was prepared by boiling *m*-nitrobenzoylanthranilic acid with excess of acetic anhydride and recrystallizing the crude product from fresh acetic anhydride. It forms small colorless, or cream-colored, needles, melting at 167–8° (cor.). It is hydrolyzed by hot dilute hydrochloric acid, but not readily by boiling water.

Calculated for $C_{14}H_8O_4N_2$:	N, 10.44.
Found:	N, 10.53.

p-Nitrobenzoylanthranil, prepared in a similar manner, crystallizes from acetic anhydride in light yellow needles, melting at 207° (cor.), hydrolyzed by hot dilute hydrochloric acid, but not readily by boiling water.

Calculated for $C_{14}H_8O_4N_2$:	N, 10.44.
Found:	N, 10.45.

II. Condensations with Acetanthranil.

2-Methyl-3-m-aminophenyl-4-quinazolone, $\overline{CH_3C : N.C_6H_4.CO.NC_6H_4NH_2}$-(*m*-).—Two grams *m*-phenylenediamine hydrochloride in aqueous solution were treated with the calculated amount of sodium hydroxide, and a gram and a half of acetanthranil added to the solution. The anthranil

[1] Friedländer and Wleügel, *Loc. cit.*; Anschütz and Schmidt, *Ber.*, 35, 4373 (1902); Heller, *Ibid.*, 36, 2766 (1903); Bamberger, *et al.*, *Ibid.*, 36, 822 (1903), and 42, 1649 (1909); Heller and Fiesselmann, *Ann.*, 324, 134 (1902).

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dissolved instantly. The solution was evaporated to dryness, the residue extracted with 95 per cent. alcohol and the alcoholic solution concentrated to crystallization. Yield, 0.5 g. The crystals obtained were recrystallized from dilute alcohol, dried at 110° and analyzed:

Calculated for $C_{15}H_{13}ON_3$: C, 71.71; H, 5.18; N, 16.73.
Found: C, 71.77; H, 5.26; N, 16.75.

A better method for the preparation of the above substance is the following: An equimolecular mixture of acetanthranil and *m*-phenylenediamine is heated to fusion and kept at the temperature of initial fusion for about five minutes. The product is finely pulverized, washed thoroughly with dilute sodium hydroxide solution, then with water, is redissolved in dilute hydrochloric acid, the solution filtered, the filtrate reprecipitated with sodium hydroxide, the precipitate washed thoroughly with water and dried. It is then usually sufficiently pure for the preparation of azo dyes. If desired, it can be further purified, as noted above, by recrystallization from dilute alcohol. Yield, 70–80 per cent. of the theory.

Carefully purified and dried over alkali *in vacuo*, it can be obtained practically colorless. As usually prepared, it forms crystals resembling wheat beards in shape and color. It melts at 210° (cor.), is very slightly soluble in water, but easily soluble in 95 per cent. alcohol or in dilute hydrochloric acid.

In one experiment, an aqueous solution of *m*-phenylenediamine was treated with acetanthranil and the product crystallized from alcohol as usual. The quinazolone was thus obtained in crystals, but on diluting the mother-liquor a different substance separated. This other compound was recrystallized from dilute alcohol, and then melted at 158° (cor.). It contained 10.22 per cent. nitrogen, while the amide intermediate in the quinazolone condensation contains 15.61 per cent. nitrogen. It was not identified.

Two grams of the 2-methyl-3-*m*-aminophenyl-4-quinazolone were dissolved in 4 cc. water and 1.5 g. concentrated sulfuric acid, 10 cc. more water added, the solution cooled to 0° and diazotized with the calculated amount of sodium nitrite using starch paper as indicator. The resultant diazo solution was warmed for an hour on the water bath. Nitrogen was evolved and the solution turned dark red. It was heated to boiling, filtered boiling hot, and the filtrate neutralized. On cooling, a yellow amorphous mass separated, slightly soluble in water, soluble in caustic alkalies to a deep red solution, and also dissolving in acids. It could not be crystallized or purified and was not further investigated. In addition to the above, a small amount of an insoluble substance was formed in the reaction.

2-Methyl-3-p-aminophenyl-4-quinazolone. — *p*-Phenylenediamine hydro-

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chloride was dissolved in water, a slight excess of potassium hydroxide added, and then slightly less than the calculated amount of acetanthranil. On warming the solution, the quinazolone separated in plates of a faint pinkish gray cast, melting at 220° (cor.). Yield, two grams from two grams anthranil. By fusing together the free diamine and the acetanthranil, as described above for the meta compound, a much larger yield (80–90 per cent. of the theory) can be secured.

Calculated for $C_{15}H_{13}ON_3$: N, 16.73.
Found: N, 16.82.

The compound is very slightly soluble in water or in dilute caustic alkalies, easily soluble in 95 per cent. alcohol or in dilute hydrochloric acid. From alcohol, it often separates as a gray powder. Freshly precipitated from acid solution and dried carefully *in vacuo* over alkali, it can be obtained practically colorless.

3,3'-p-Phenylene-bis-(2-methyl-4-quinazolone),

$$CH_3C : N.C_6H_4.CO.N(1)C_6H_4(4)N.CO.C_6H_4.N : CCH_3.$$

A small amount of this diquinazolonyl was found in one of the above *p*-phenylenediamine condensations. It was easily separated from the *p*-aminophenylquinazolone as it is much less soluble in alcohol. It crystallized from a large volume of hot alcohol in colorless, microscopic crystals, melting above 300°.

Calculated for $C_{24}H_{18}O_2N_4$: N, 14.20.
Found: N, 14.17.

It is insoluble in water and dissolves in alcohol with difficulty. In other experiments, *p*-phenylenediamine was fused with excess of acetanthranil without the formation of any appreciable amount of the diquinazolonyl compound.

2-Methyl-3-m-aminotolyl-4-quinazolone,

$$CH_3C : N.C_6H_4.CO.NC_6H_3(NH_2)(m\text{-})CH_3(o\text{-, or } p\text{-}).$$

An equimolecular mixture of acetanthranil and 2,4-diaminotoluene was gradually heated on the sand bath until the mass boiled. When cool the glassy melt was pulverized, dissolved in dilute hydrochloric acid, the solution filtered, and the filtrate precipitated by potassium hydroxide. The sticky precipitate slowly hardened. It was then powdered, washed thoroughly with water, and crystallized from dilute alcohol. Minute colorless needles were thus obtained, melting at 132.4° (cor.).

Calculated for $C_{16}H_{15}ON_3$: N, 15.8.
Found: N, 15.7.

Acetanthranilic m-aminotoluidide,

$$(1)CH_3CONHC_6H_4(2)CONHC_6H_3(NH_2)(m\text{-})CH_3(o\text{-, or } p\text{-}).$$

In another experiment, an equimolecular mixture of 2,4-diaminotoluene and acetanthranil was gently fused, the product washed with dilute potas-

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sium hydroxide solution, dissolved in dilute hydrochloric acid, filtered, the filtrate reprecipitated by alkali, the precipitate washed and recrystallized from alcohol. Stellate groups of colorless needles resulted, melting at 137–8° (cor.), insoluble in water, but easily soluble in alcohol.

Calculated for $C_{16}H_{17}O_2N_3$: N, 14.84.
Found: N, 14.68.

We have not determined the position of the methyl group in this or the foregoing compound, so that we do not know which of the two amino groups took part in the condensation.

2-Methyl-3-p-aminotolyl-4-quinazolone,

$$CH_3C : N.C_6H_4.CONC_6H_3(NH_2)(p\text{-})CH_3(o\text{-, or } m\text{-}),$$

was prepared in a manner entirely similar to that employed for the *m*-aminotolyl compound, using 2,5- instead of 2,4-diaminotoluene, the diamine being first carefully purified by recrystallization from ethyl acetate.

Calculated for $C_{16}H_{15}ON_3$: N, 15.8.
Found: N, 15.9.

The pure substance forms minute crystals, rather darker than those of its isomer, and melting at 169° (cor.).

2-Methyl-3-[4′-aminodiphenyl]-4-quinazolone,

$$CH_3C : NC_6H_4CON(4)C_6H_4.C_6H_4NH_2(4').$$

1.6 g. benzidine and 1.5 g. acetanthranil were gently fused together. The mass quickly set to a compact brown solid. The temperature was kept at the point of initial fusion for about five minutes. The cold melt was finely pulverized, washed with dilute potassium hydroxide solution, then with water, dissolved in dilute hydrochloric acid, the solution filtered, the filtrate precipitated with potassium hydroxide, the precipitate washed with water and dried. Yield, 2.2 g. In later experiments, the yield was raised to 90–100 per cent. of the theory.

Calculated for $C_{21}H_{17}ON_3$: N, 12.84.
Found: N, 12.70.

The substance burns with considerable difficulty. As thus obtained, the compound is generally a pale yellow or brownish powder, m. p. 282–3° (cor.), moderately soluble in 95 per cent. alcohol, very slightly soluble in water, but dissolving easily in dilute hydrochloric acid.

2-Methyl-3-[4′-aminoditolyl]-4-quinazolone,

$$CH_3C:NC_6H_4CON(4)C_6H_3(3)(CH_3).C_6H_3(3')(CH_3)(4')(NH_2),$$

was prepared from *o*-tolidine and acetanthranil in essentially the same manner as the benzidine compound above. Yield, about 90 per cent.

Calculated for $C_{23}H_{21}ON_3$: N, 11.83.
Found: N, 11.69.

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The pure substance is practically colorless. As usually obtained, it is a pale brownish powder, m. p. 80–1° (cor.). This drop of 200° in melting-point as compared with the benzidine compound is rather surprizing. The substance is very slightly soluble in water, but easily dissolves in 95 per cent. alcohol or in dilute hydrochloric acid.

2-Methyl-3-[4'-aminoethoxydiphenyl]-4-quinazolone,

$CH_3C : NC_6H_4CON(4)C_6H_3(3)(OC_2H_5).C_6H_4NH_2(4)'$, or

$CH_3C : NC_6H_4CON(4)C_6H_4.C_6H_3(3')(OC_2H_5)(4')(NH_2)$.—

One molecule ethoxybenzidine and slightly more than one molecule acetanthranil were fused together in an oil bath. The product was washed with boiling potassium hydroxide solution (1 : 2) and then allowed to cool. When cold it was finely pulverized, washed with water, and purified as already described for the benzidine compound. Dried over sulfuric acid and analyzed, the following figure was obtained:

Calculated for $C_{23}H_{21}O_2N_3$: N, 11.32.
Found: N, 11.31.

Brownish powder, m. p. 86–7° (cor.), very slightly soluble in water, readily soluble in 95 per cent. alcohol or in dilute hydrochloric acid. The location of the ethoxy group has not been determined definitly.

2-Methyl-3-[4'-aminodianisyl]-4-quinazolone,

$CH_3C : NC_6H_4CON(4)C_6H_3(3)(OCH_3).C_6H_3(3')(OCH_3)(4')(NH_2)$.—

An equimolecular mixture of acetanthranil and *o*-dianisidine was fused at 100°. The black melt was dissolved in alcohol and the solution diluted with water. The precipitate which separated was dissolved in dilute hydrochloric acid, the solution filtered and reprecipitated with dilute alkali. This precipitate was washed thoroughly and dried in a desiccator over sulfuric acid. Yield, 95–100 per cent.

Calculated for $C_{32}H_{21}O_3N_3$: N, 10.85.
Found: N, 11.04.

The compound is light colored and crystallin when freshly prepared, but quickly darkens. It is insoluble in water, but easily soluble in alcohol or in dilute mineral acids, giving very dark solutions. It melts at 72–3° (cor.).

III. Condensations with Substituted Acetanthranils.

2-Methyl-6-bromo-3-p-aminodiphenyl-4-quinazolone,

$CH_3C : NC_6H_3BrCO.N.C_6H_4.C_6H_4NH_2(4')$,

prepared by heating together 5-bromoacetanthranil and benzidine, forms a light brown powder, melting at 198–9° (cor.), insoluble in water or in aqueous solutions of alkalies, and not readily soluble in dilute hydrochloric

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acid. It diazotizes readily, the diazonium salts being difficultly soluble.

2-Methyl-6-nitro-3-p-aminophenyl-4-quinazolone,

$$\overline{CH_3C : NC_6H_3(NO_2)CO.N.C_6H_4NH_2(p)},$$

prepared by fusing together an equimolecular mixture of 5-nitroacetanthranil and *p*-phenylenediamine, was obtained as a dark brown powder, melting with apparent decomposition at 259–60° (cor.), and dissolving easily in dilute hydrochloric acid or in 95 per cent. alcohol.

Not enough of either of the above substances was available for an analysis, but there seems no reason for assuming that the condensation in these cases followed any other course than that already described for similar mixtures.

2-Methyl-6-acetamino-3-p-aminophenyl-4-quinazolone,

$$\overline{CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4NH_2(p)},$$

was prepared in the same way as the corresponding 7-acetamino body (which follows) and shows similar properties. It was purified by solution in dilute hydrochloric acid and reprecipitation with potassium hydroxide. The purplish precipitate thus thrown down softens and shrinks together somewhat at 170–5°, and melts at about 280° (uncor.).

Calculated for $C_{17}H_{16}O_2N_4$:	N, 18.18.
Found:	N, 18.06.

2-Methyl-7-acetamino-3-m-aminophenyl-4-quinazolone.—An equimolecular mixture of 4-acetaminoacetanthranil and *m*-phenylenediamine was heated gradually. It first softened, then hardened again, solidifying at about 110°. Dissolved in dilute hydrochloric acid and reprecipitated with potassium hydroxide, it came down in an amorphous, colorless form, gradually browning on standing, and was quite sticky. Dried thoroughly in a desiccator, it melted above 310° (cor.).

Calculated for $C_{17}H_{16}O_2N_4$:	N, 18.18.
Found:	N, 18.3.

2-Methyl-7-acetamino-3-p-aminophenyl-4-quinazolone.—An equimolecular mixture of 4-acetaminoacetanthranil and *p*-phenylenediamine was heated in the oil bath with constant stirring. At 80–100° the mass became sticky, at 100–10° most of the reaction was completed. The mass does not melt then even if carried up to 195°. The dark-colored product when cold was pulverized fine, washed with ten per cent. sodium hydroxide solution, then with water, redissolved in dilute hydrochloric acid filtered, the filtrate made alkaline with sodium hydroxide, the precipitate filtered out, washed thoroughly with water and dried. It is a dark purplish blue powder, melting above 360°, slightly soluble in cold water, readily soluble in 95 per cent. alcohol, soluble in dilute mineral acids, and but very slightly soluble in dilute aqueous caustic

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alkalies. It is strongly triboelectric. From 2 g. of the anthranil, 2.85 grams of the crude condensation product (before re-solution and re-precipitation) were secured.

Calculated for $C_{17}H_{16}O_2N_4$: C, 66.23; H, 5.20; N, 18.18.
Found: C, 65.83; H, 5.26; N, 18.40.

2-Methyl-7-amino-3-p-aminophenyl-4-quinazolone.—The above acetyl derivative was boiled with excess of dilute (20 per cent.) hydrochloric acid for three hours and the purple solution then made alkaline with sodium hydroxide. The free base separated as a dark bluish precipitate which became crystallin on standing. It was purified by re-solution in dilute hydrochloric acid and reprecipitation with alkali, the pure substance melting at 287° (cor.). Its solubilities are about the same as those of the acetyl derivative and it, too, is triboelectric.

Calculated for $C_{15}H_{14}ON_4$: N, 21.05.
Found: N, 20.97.

2-Methyl-7-acetamino-3-aminotolyl-4-quinazolone,

$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(NH_2)(m)(CH_3)(o, \text{ or } p)$.—An intimate mixture of 0.3 gram 2,4-diaminotoluene and 0.5 gram 4-acetaminoacetanthranil was carefully heated. At 70° the mass became adhesive, and at 100° it fused to a thick paste. The temperature was finally raised to 115°. The crude product was purified as described above, the pure substance being light brown and melting at 290° (cor.).

Calculated for $C_{18}H_{18}O_2N_4$: N, 17.39.
Found: N, 17.59.

In order to determin in what position the quinazolone was united to the toluidine molecule, some of the above compound was boiled with excess of acetic anhydride. The substance dissolved easily in the hot anhydride and minute, colorless needles separated on cooling the solution. Recrystallized thrice from alcohol, it melted at 268.5° (cor.), and was decidedly triboelectric. On analysis, it was found to contain 14.1 per cent. nitrogen. This does not correspond to any simple acetylation product. The diacetyl derivative contains 15.4 per cent. nitrogen, the triacetyl 13.8, and the tetraacetyl 12.5. Dried for three hours at 130–60° and again analyzed, 14.53 per cent. nitrogen was found. Recrystallized from acetic anhydride and analyzed once more, 14.3 per cent. nitrogen was obtained. As the purpose of the acetylation was the protection of the amino group during oxidation, it was decided to proceed with the oxidation without further attempts to purify the acetylation product. 3.5 grams of it, 7 grams magnesium sulfate, and 500 cc. of water, were mixed in a flask with return condenser and the mixture heated to boiling. 7 grams potassium permanganate were added gradually to the boiling solution (during one and a half hours), and after two hours' boiling the solution was allowed to cool and the precipitated manganese oxide filtered

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out. A portion of the filtrate acidified with hydrochloric acid gave a turbidity which cleared on further addition of the acid with evolution of carbon dioxide. Acetic acid gave similar results. The filtrate was therefore carefully treated with dilute acetic acid until it became turbid, and the turbid solution then let stand. In a day or two a small amount of sticky precipitate separated from this turbid solution, leaving the supernatant liquid clear. The amount of the precipitate was too small to carry the investigation further.

2-Methyl-7-amino-3-aminotolyl-4-quinazolone.—The acetyl group was split off the above 7-acetamino compound by boiling it for an hour with ten per cent. hydrochloric acid. The free base was precipitated by alkali as a sticky paste. Purified, washed and dried, it melts at 262° (cor.).

Calculated for $C_{16}H_{16}ON_4$: N, 20.0.
Found: N, 19.95.

2-Methyl-7-acetamino-3-[4′-aminodiphenyl]-4-quinazolone,

$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4.C_6H_4NH_2(4')$.—An equimolecular mixture of 4-acetaminoacetanthranil and benzidine was gradually heated. The mixture became pasty and adhesive at 100°, then hardened. On treating the crude product with dilute hydrochloric acid, a considerable amount remained insoluble. The soluble constituent was reprecipitated by alkali and dried in an air bath (causing it to darken). It decomposes at 296–7° (cor.).

Calculated for $C_{23}H_{20}O_2N_4$: N, 14.58.
Found: N, 14.70.

The product insoluble in hydrochloric acid melts with decomposition at 256° (cor.). Found: N, 12.31. This figure corresponds to the diquinazolonyl compound (*i. e.*, one molecule of the diamine condensed with two of the anthranil), $CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4.C_6H_4.N.CO(CH_3CONH)C_6H_3N : CCH_3$, with six molecules of water, but not enough of the material was separated to study it further.

2-Methyl-7-acetamino-3-[4′-aminoditolyl]-4-quinazolone,

$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(3)(CH_3).C_6H_3(3')(CH_3)(4')(NH_2)$.—An equimolecular mixture of 4-acetaminoacetanthranil and *o*-tolidine was heated gradually to 150°. At 110° the mixture became adhesive, and pasty at 120–5°. The resultant brown paste was purified as usual and a product obtained melting at about 105°.

Calculated for $C_{23}H_{24}O_2N_4$: N, 13.59.
Found: N, 13.35.

The substance does not crystallize well from 95 per cent. alcohol. It was dissolved in hot alcohol, water added to turbidity and the solution

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allowed to cool. The substance separated in an amorphous sticky condition. Dried and pulverized, it formed a light brown powder, melting at about 95°, darkening and decomposing at 120–5°.

Calculated (as above): N, 13.59.
Found: N, 13.34.

2-Methyl-7-acetamino-3-[ethoxy-4'-diphenyl]-4-quinazolone,

$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(OC_2H_5)(3).C_6H_4NH_2(4')$, or

$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4.C_6H_3(3')(OC_2H_5)(4')(NH_2)$.—An equimolecular mixture of 4-acetaminoacetanthranil and ethoxybenzidine was heated gradually to 150°. At 100° the mixture softened and became pasty at 130°. The crude product after purification in the usual way, melted at about 105–10°, and decomposed at about 120–5°.

Calculated for $C_{25}H_{24}O_3N_4$: N, 13.08.
Found: N, 12.56, 12.43.

As the wide melting points and low analytical results indicate, we probably failed in this case to get a pure product.

2-Methyl-7-acetamino-3-[4'-aminodianisyl]-4-quinazolone,

$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(3)(OCH_3).C_6H_3(3')(OCH_3)(4')(NH_2)$.—An intimate mixture of 1.2 grams each 4-acetaminoacetanthranil and di-*o*-anisidine was heated carefully. At 85° it became slightly sticky, at 120° pasty. It was finally heated to 140° and then allowed to cool. The crude product dissolved in hydrochloric acid and reprecipitated with alkali separated as a white, flocculent precipitate, which gradually turned purplish. It was further purified by re-solution and reprecipitation, and then showed a melting point of about 144°.

Calculated for $C_{25}H_{24}O_4N_4$: N, 12.61.
Found: N, 12.23.

This unsatisfactory analytical result was due to the difficulty in thoroughly purifying the substance.

We therefore acetylated the compound with acetic anhydride, and crystallized the product twice from alcohol, getting a substance melting at 239° (cor.), which is apparently the tetraacetyl compound:

Calculated for tetraacetyl compound ($C_{31}H_{33}O_7N_7$): N, 9.83.
Found: N, 9.92.

IV. Condensations with Benzoylanthranils.

Benzoylanthranil and Ammonia.—Anschütz, Schmidt and Greiffenberg[1] passed ammonia into a boiling absolute alcohol solution of benzoylanthranil and obtained the *o*-benzoylaminobenzamide, melting at 214-5° with decomposition.

[1] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3484 (1902).

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We boiled benzoylanthranil with excess of strong aqueous ammonia and recrystallized from alcohol the white solid which separated. Minute, colorless crystals were thus obtained, which softened at 108° (cor.) and melted to a turbid liquid at 118° (cor.), the melt becoming clear at a slightly higher temperature. From what follows, it seems probable that this is the secondary amide combination:

Calculated for $(C_6H_5CONHC_6H_4CO)_2NH$: N, 9.09.
Found: N, 9.09.

Boiled with potassium hydroxide solution, it dissolved and, on acidifying the solution, long silky needles of 2-phenyl-4-quinazolone (m. p. 237.5° (cor.)) separated, a compound already in the literature.[1]

Benzoylanthranil and p-Phenetidine.—The two were mixed dry in molecular proportion and the mixture boiled for several minutes. On cooling, the mass solidified. It was washed with alcohol, and then appeared in minute colorless crystals, melting at 213° (cor.), very difficultly soluble in alcohol. It has not been further investigated.

Benzoylanthranils and Aromatic Diamines.—Benzoylanthranil, *m*- and *p*-nitrobenzoylanthranils, were fused with *m*- and *p*-phenylenediamines. The products were insoluble in acids or alkalies, slightly soluble in alcohol, and could not be diazotized. It seems unlikely, therefore, that they were the desired quinazoline condensations. Judging by the nitrogen determinations in the case of the *m*- and *p*-nitro derivatives, the products are the diquinazolonyls. No aminoaryl quinazolones were isolated.

3,3′-m-Phenylene-bis[*2-m-nitrophenyl-4-quinazolone*],

$$O_2NC_6H_4.\overline{C : NC_6H_4CO.N(1)C_6H_4(3)N.COC_6H_4N : C}.C_6H_4NO_2.$$

—An equimolecular mixture of *m*-nitrobenzoylanthranil and *m*-phenylenediamine was fused and then allowed to cool. The mass was powdered, and warmed first with dilute and then with concentrated hydrochloric acid. Little, if anything, was dissolved by this treatment. It was then washed thoroughly with water, then with strong sodium hydroxide solution (to remove any acetanthranilic acid), and again with water, and dried.

As thus purified, it is a yellowish powder, practically insoluble in water, alcohol, ethyl acetate or benzene. On heating, it darkens and shrinks at 180°, finally melting at 226°.

Calculated for $C_{34}H_{20}O_6N_6$: N, 13.81.
Found: N, 14.02.

3,3′-m-Phenylene-bis-[*2-p-nitrophenyl-4-quinazolone*], prepared in similar manner, using the *p*-nitrobenzoylanthranil instead of the meta isomer, was likewise obtained as a yellow insoluble powder.

[1] Körner, *J. prakt. Chem.*, [2] 36, 155 (1887); Bischler and Lang, *Ber.*, 28, 289 (1895); Anschütz, Schmidt and Greiffenberg, *Loc. cit.*

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Calculated for $C_{31}H_{20}O_6N_6$: N, 13.81.
Found: N, 14.0.

It melts at 207°. Boiled with hydrochloric acid, it turns white but does not dissolve.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

PSEUDO ACID ESTERS IN THE MESOXALIC ESTER SYNTHESIS.[1]

BY RICHARD SYDNEY CURTISS AND JOHN ANTON KOSTALEK.

Received March 25, 1911.

In a synthesis of mesoxalic esters which was discovered by one of us and reported in the *American Chemical Journal*,[2] the red oxides of nitrogen were allowed to act an malonic ester at —10°. The ethyl mesoxalate produced was removed by distillation and the residual oil was found to contain a high percentage of nitrogenous esters, having acid properties, and which produced with alcoholic potash a yellow salt. The analysis showed this salt to contain a percentage of potassium according well with that of the salt of ethyl isonitrosomalonate, $K–O–N=C=(CO_2C_2H_5)_2$, and it was at first supposed to be this compound. Isonitrosomalonic acid was made by Baeyer,[3] who found that its aqueous solution decomposes at 40° into hydrocyanic acid, carbon dioxide, and water. Conrad and Bischoff[4] confirm this result.

It was noticed at that time that no odor of prussic acid was apparent when the yellow potassium salt was boiled with alkali to saponify the ester, and subsequently heated with hydrochloric acid to liberate and decompose the isonitrosomalonic acid. The results of the test were therefore not in accordance with this characteristic of the potassium salt of isonitrosomalonic acid. The complete analysis of this salt, later, showed that it was not a derivative of ethyl isonitrosomalonate, and we wish therefore to correct the statements made in the former paper[5] concerning the identity of this salt, and in accordance with the results herein presented.

This investigation was begun by the senior author, and Mr. Ruric Creegan Roarke, to whom we owe much for the initial experiments and attempts in separating and studying the potassium salts of ethyl nitromalonate and ethyl dinitroacetate. Our primary idea was the study

[1] Abstract of a thesis presented by Mr. Kostalek to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Curtiss, *Am. Chem. J.*, 35, 477.

[3] *Ann.*, 131, 293.

[4] *Ibid.*, 209, 211.

[5] *Ibid.*, 35, 478, 482, 483.

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of the mechanism of the reactions which take place in the mesoxalic ester synthesis when malonic esters are treated with "nitrous anhydride." The oxidation of the methylene hydrogen atoms of ethyl malonate to hydroxyl groups, $\begin{matrix}H\\H\end{matrix}\!\!>\!C=(CO_2R)_2 + O_2 \longrightarrow \begin{matrix}HO\\HO\end{matrix}\!\!>\!C=(CO_2R)_2$, yielding ethyl dihydroxymalonate appears very simple; but the investigation has shown that a number of other products are formed which contain nitrogen attached to the methylene carbon, and some of these have acid properties. It was further found that there was a direct relation between the amount of mesoxalic ester produced and the yield of these nitrogenous esters, and that the yield of the former varied inversely with the amount of the latter present. Some of these nitrogenous derivatives are quite unstable, and undergo sudden, and at times almost explosive decomposition, during the process of distillation *in vacuo*, which is used to separate the mesoxalic ester. These facts led us to believe that they might be the intermediate compounds, in this synthesis, from which mesoxalic ester was obtained by elimination of the groups containing nitrogen. This idea was confirmed when it was found that the yield of ethyl oxomalonate, $OC=(CO_2C_2H_5)_2$, was decidedly increased when the "crude oil," obtained by the action of the red oxides of nitrogen on ethyl malonate, was directly distilled *in vacuo*, whereas the yield of the nitrogenous esters was increased, and less of the mesoxalate obtained, when they were separated by extraction with water. In this treatment of the "crude oil" with water the mesoxalic ester goes into the water and may be recovered by extraction with ether, while the nitrogenous ester derivatives remain undissolved. When the latter are distilled *in vacuo*, partial decomposition takes place yielding much nitrogen and nitric oxide, nitrogen peroxide, carbon dioxide, alcohol and other organic products.

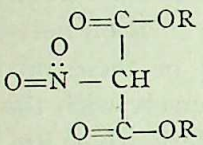
In investigating these acid esters containing nitrogen we have separated, by means of their potassium salts, two oils having acid properties. They have been identified as ethyl nitromalonate, $O_2N-C=(CO_2C_2H_5)_2$, and ethyl dinitroacetate, $\begin{matrix}O_2N\\O_2N\end{matrix}\!\!>\!C(H)-CO_2C_2H_5$.

The separation of these two potassium salts has been slow and difficult, owing to their instability, the slight difference in their solubilities, and the fact that they are readily decomposed when their solutions are heated, and often explode in the combustion tube when burned. We have prepared the pure potassium salt of each of the above pseudo acids as well as some of the salts with ammonia, hydrazine, aniline, sodium and silver. All of these occur in the colored form. From the pure potassium salts we have regenerated the pseudo acids and analyzed them. A peculiar

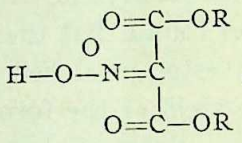
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interest attaches to these acid oils inasmuch as they are colorless, but yield colored alkali salts. Some of these salts exist in two forms, the colorless, the yellow, or the red. These interesting facts of color were investigated by Hantzsch and formed a part of his celebrated work upon the "pseudo acids"[1] and "chromo-isomers." He explains the appearance of color in the potassium salt of ethyl nitromalonate, $O_2N—C=(CO_2C_2H_5)_2$, by a molecular rearrangement of the pseudo acid into the "aci" form,

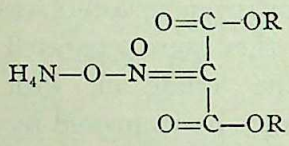


Pseudo acid, colorless.

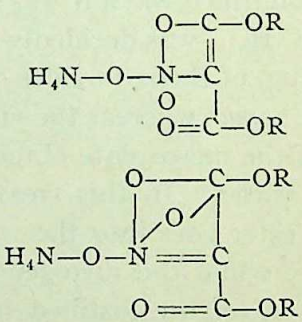


Leuco "Aci" form, colorless.

and as the nitro group is not a chromophore[2] it becomes so only when interacting with an adjacent carbonyl, or nitro group,[3] as illustrated below. The possibility of such colored or "chromo" isomers is here shown, with the ammonium salt of ethyl nitromalonate,[4] which we have made in both the leuco and colored forms:



Leuco form.



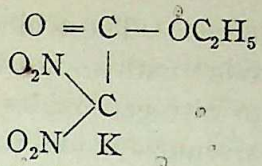
Chromo forms.

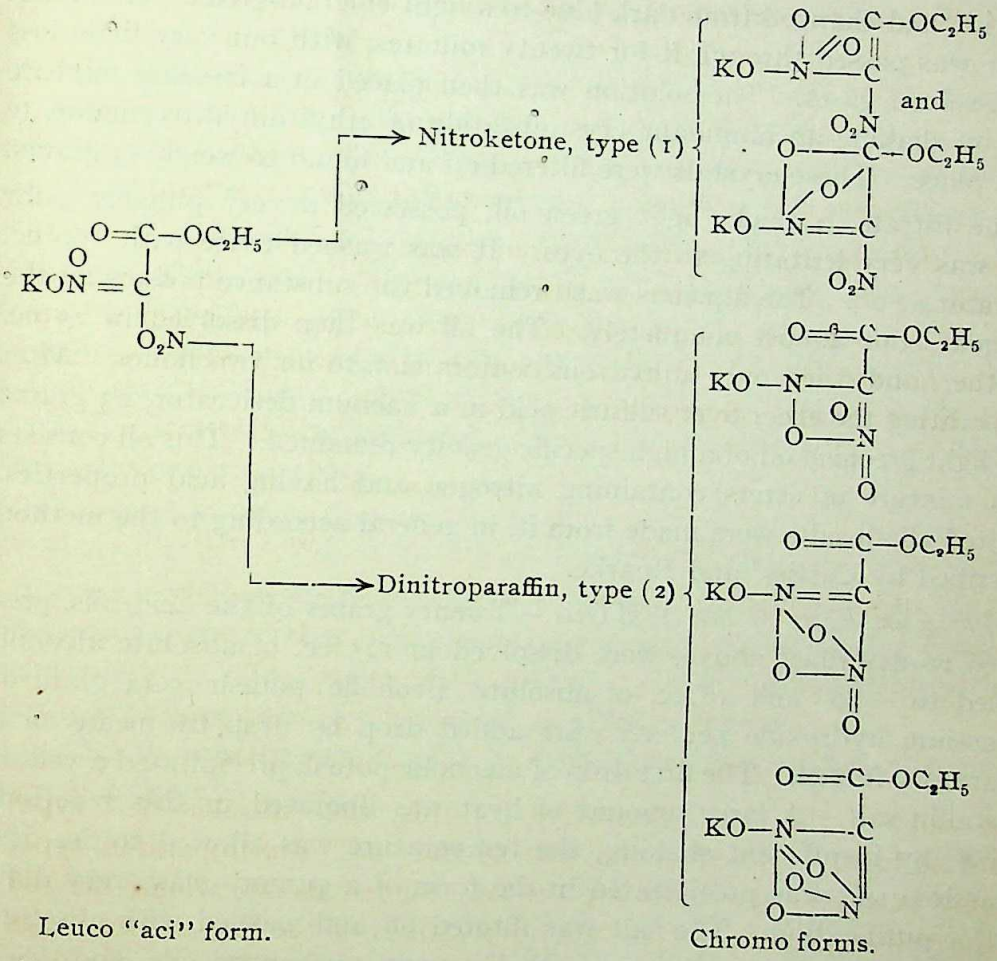
The salts of the "aci" derivatives of this, the "nitroketone," type[5] are not as highly colored as the salts of the "aci" dinitroparaffin type, and only in a very few cases are the two colored modifications, the red and the yellow, known. The "aci" derivatives of the first-named series can, in most cases, be easily obtained in the leuco form. Thus, ammonium ethyl nitromalonate, $H_4NO.ON=C(COOC_2H_5)_2$, can be obtained in the leuco form by recrystallization of the yellow chromo form from absolute alcohol. Dissolved in water, hot or cold, or in absolute alcohol, the leuco ammonium ethyl nitromalonate yields a yellow solution, indicating that in solution the leuco ion is not stable and changes into the chromo ion, but may be deposited in the leuco form as it separates out.

[1] *Ber.*, 32, 578, 579, 583; 35, 1001; 40, 1523.
[2] *Ibid.*, 39, 1084, 1096.
[3] *Ibid.*, 32, 578, 610, 626; 39, 3150; 40, 1533.
[4] See Hantzsch, *Ber.*, 40, 1523.
[5] *Ibid.*, 40, 1535, 1536.

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In potassium ethyl dinitroacetate,  , with two nitro groups and a carbonyl group linked to the same carbon atom, both the nitroketone type and "aci" dinitroparaffin type[1] of rearrangement, suggested by Hantzsch, are possible, five colored isomers in all.



Two of these forms only are known: the yellow, more stable form, probably of type (1), and the red form probably of type (2) which is known only in solution. The cold aqueous solution of the yellow form is likewise yellow, but changes to red when heated, and again reverts to the original color when cooled. The two forms exist in solution as an equilibrium mixture, the amount of each varying with the temperature. The changing color indicates change of structure. The solution in absolute alcohol remains yellow even when heated to boiling.

Experimental.

Preparation of the Pseudo Acid Oils by the Action of Nitrogen Oxides

[1] *Ber.*, 40, 1535, 1536.

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on Ethyl Malonate.—These oils were prepared according to the method used by Curtiss,[1] with some slight modifications.

A stream of nitrogen oxides, prepared by the action of nitric acid, sp. gr. 1.42, on arsenious oxide, was passed into 50 cc. of malonic ester kept at —10° to —15°. In twenty minutes the mass had increased 88 grams in weight. It was then packed in ice and allowed to warm slowly, over a period of seventeen hours, to room temperature. The color of the solution had changed from dark blue to a light emerald-green. A current of air was passed through it for twenty minutes, with but very little loss of dissolved gases. The solution was then placed in a freezing mixture and on shaking an abundant crystallization of ethyl dihydroxymalonate took place. These crystals were filtered off and found to weigh 23 grams.

The filtrate, a thick, light green oil, possessed a very pungent odor, and was very irritating to the eyes. It was washed twice with 100 cc. of water at 0°. The aqueous wash removed the substance possessing the pungent odor almost completely. The oil was then dissolved in 25 cc. of ether, and dried over anhydrous sodium sulfate for two hours. After evaporating the ether over sulfuric acid in a vacuum desiccator, 23 grams of a light greenish oil of a high specific gravity remained. This oil consists of a mixture of esters containing nitrogen and having acid properties. Colored alkali salts were made from it, in general according to the method described by Curtiss[2] and Roarke.[3]

Potassium Salts of the Acid Oils.—Twenty grams of the acid oils, prepared as described above, were dissolved in 125 cc. of absolute alcohol, cooled to —10° and 46 cc. of absolute alcoholic potash (0.14 gram of potassium hydroxide per cc.) were added drop by drop, by means of a separatory funnel. The first drop of alcoholic potash precipitated a yellow crystallin salt. A large amount of heat was liberated in this reaction, and if, by insufficient shaking, the temperature was allowed to rise, the potassium salt was precipitated in the form of a gummy mass very difficult of purification. The salt was filtered off and washed with absolute alcohol to remove the excess of alkali or any unchanged oils, and dried in a vacuum desiccator. Nineteen grams of a yellow salt were thus obtained. This product is a mixture composed chiefly of the salts of ethyl dinitroacetate and ethyl nitromalonate.

In the preparation of these potassium salts of the "crude acid oil," the first few drops of alcoholic potash, in some cases, produced a deep red coloration, which would suddenly disappear and the precipitation of the yellow potassium salts immediately follow. This coloration is perhaps due to the temporary formation of the red modifications of ethyl dinitroacetate

[1] *Am. Chem. J.*, 25, 478.

[2] *Ibid.*

[3] Thesis for the degree of M. A. in Chemistry, University of Illinois, 1908, p. 5.

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and potassium ethyl nitromalonate, or it may indicate the presence of ethyl nitrolic acetate[1] $HON = C(O_2N)—CO_2C_2H_5$. This compound gives a red color in alkaline solutions as do all nitrolic acids. Being unstable, and easily decomposed by water, the red color is soon lost.

Separation of the Potassium Salts of the Acid Oils; Potassium Ethyl Dinitroacetate, $K—O—N = C(O_2N) — CO_2C_2H_5$.—Thirty-three grams of the crude, yellow potassium salts, prepared as just described, were dissolved in 60 cc. of hot water. The solution was deep red when hot, becoming greenish yellow when cold. When cooled the potassium salts crystallized out in the form of greenish yellow needles. These were filtered off, washed with 15 cc. of absolute alcohol and 5 cc. of ether. Yield, 17 grams. Decomposing point, 190°. This was mostly potassium ethyl dinitroacetate. On recrystallizing it three times from hot 95 per cent. alcohol, it was obtained in the form of greenish yellow, almost colorless needles, with a constant decomposing point of 194–195°, when immersed in the bath at 180°. It was finely powdered, dried over sulfuric acid in a vacuum desiccator and analyzed.

Calculated for $C_4H_5N_2O_6K$: K, 18.05 ; H, 2.31 ; N, 12.96 ; C, 22.22.
Found: K, 18.06, 18.01; H, 2.70, 2.65; N, 13.24, 12.96; C, 22.62, 22.52.

Curtiss and Roarke[2] determined the molecular weight of this salt by the boiling-point method, using acetone as a solvent, and by the freezing-point method, using water as a solvent. These determinations show that it is unimolecular and is ionized in water solutions.

(*a*) By the freezing-point method, using water as a solvent, the results were as follows:

	s. Gram.	S. Gram.	*d.*	Mol wt.
I	0.2009	44.89	0.0800	103.5
II	0.5017	44.89	0.1830	112.9
III	0.7097	44.89	0.2500	116.9

(*b*) By the boiling-point method, using acetone as a solvent, the results were as follows:

	s. Gram.	S. Gram.	*r.*	Mol. wt.
I	0.1856	15.72	0.0800	246.4
II	0.4427	15.72	0.2100	224.0
III	0.6000	15.72	0.2600	245.1

Calculated molecular weight of $C_4H_5O_6N_2K$, 266.2. The crystals of the pure potassium salt are a very pale greenish yellow and are in the form of fine monoclinic prisms. It sometimes separates out

[1] *Ber.*, 28, 1215.
[2] R. C. Roarke, Master's Thesis, University of Illinois, 1908, p. 10.

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from an aqueous solution in glistening yellow plates, but when recrystallized again changes to needles. It is apparently dimorphous. Sunlight changes the salt to a darker shade of yellow. The salt suddenly explodes with purple flame when heated on a platinum spatula, or in a test tube. A hot aqueous solution of this salt is red but becomes yellow on cooling, suggesting an internal rearrangement. The above results identify this salt as that of ethyl aci-dinitroacetate, made by Bouveault and Wahl.[1]

Reduction of Potassium Ethyl Dinitroacetate.—Potassium ethyl dinitroacetate was submitted to the reducing action of dilute hydrochloric acid and granulated tin. The reaction mixture was extracted with ether and a heavy yellow viscous oil was obtained. This oil reduced Fehling's solution. With concentrated sulfuric acid and an aqueous solution of egg albumen,[2] it yielded a pink-purple solution, indicating the presence of glyoxylic acid. The aqueous extract was treated with hydrogen sulfide to remove the dissolved tin. The residue, obtained by evaporation of the aqueous filtrate, when heated with potassium hydroxide, showed the presence of ammonium salts. No hydroxylamine or hydrazine was found in the residue. The two nitro groups in the ester are here eliminated as ammonia and are replaced by oxygen, yielding glyoxylic ester.

The salt was reduced with 2 per cent. sodium amalgam in the proportion to furnish four atoms of hydrogen for one molecule of the salt. The reaction was carried out at 0°, in an aqueous solution. One-half of the hydrogen was absorbed rapidly with no smell of ammonia apparent. After this, further addition of amalgam changed the yellowish green solution momentarily red (ethyl nitrolic acetate?). An ether extract of the solution yielded a small amount of a spicy oil, which exploded violently when heated. The green aqueous solution freed of ether-soluble products suddenly became colorless, when the reduction was carried further and nitrogen was then eliminated as shown by an ammonia-like odor. The attempts to establish the presence of intermediate reduction products was not carried further.

Action of Alkyl Halides on Potassium Ethyl Dinitroacetate.—Potassium ethyl dinitroacetate does not react with ethyl or methyl iodide in the presence of 95 per cent. alcohol, or absolute alcohol, to any appreciable extent, even if heated in a sealed tube to 145° to 150°. In the presence of 50 per cent. alcohol a reaction did take place. Equimolecular quantities of potassium ethyl dinitroacetate and methyl as well as ethyl iodide were heated with 50 per cent. alcohol in a sealed tube for one hour at 100° to 110°. A yellow viscous oil was obtained by extraction of the reaction mixture with ether, which did not crystallize. This oil was formed to the extent of 20 per cent. of the potassium salt used. It was not further

[1] *Compt. rend.* 136, 159.

[2] Hopkins and Cole reaction.

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studied, because of the ease with which it decomposed when any attempt was made to purify it.

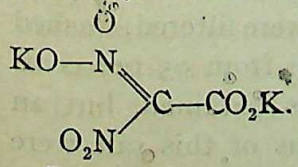
Potassium ethyl dinitroacetate reacted more readily with ethyl sulfate than with alkyl halides.

Molecular quantities of these substances were heated for thirty minutes in a sealed tube to 100°–110 with 50 per cent. alcohol. Potassium sulfate and potassium nitrite were formed in the reaction. On extraction with ether a 50 per cent. yield of heavy oil was obtained. It did not crystallize and on distillation under diminished pressure it was found to be a mixture of oils, which were not further studied because of lack of time.

The stability of this salt toward alkylation was further shown by Mr. Roarke who found that it could be boiled for several hours with benzyl chloride in a solution of 50 per cent. alcohol with no apparent change.

Saponification of Potassium Ethyl Dinitroacetate.—Three grams of this (1 mol.) were boiled for half an hour with a solution of potassium hydroxide (2 mols.) in 98 per cent. alcohol. The product was washed with hot alcohol and dried over sulfuric acid. 2.3 grams of a brilliant chrome yellow salt were obtained and recrystallized from 75 per cent. alcohol. It exploded very violently at 210°, often blowing the melting-point tube through the bottom of the flask.

The free acid was obtained from 2 grams of this salt by suspending it in 6 cc. of water and 15 cc. of ether and slowly dropping into it 14 cc. of 2 *N* sulfuric acid. It was kept at —13° and thoroughly agitated during the operation. A continuous evolution of carbon dioxide occurred until one-third of the acid had been run in. The washed ethereal solution was evaporated over sulfuric acid in a vacuum desiccator for twelve hours. An extremely unstable, limpid, yellow oil remained (0.6 g.). When taken from the vacuum which had been maintained over night it immediately began to give off a gas and to heat rapidly. It was at once replaced in the desiccator and evacuated. The reaction ceased. When air was again admitted to it a half hour later it instantly exploded with great violence, with a flash of flame followed by a dense cloud of vapors of the red oxides of nitrogen. We did not make a combustion with it. From the method of making it, and from its properties we suppose it to be dinitroacetic acid, $(O_2N)_2CH—CO_2H$, and the explosive chrome yellow salt, probably one of the chromo isomers of dipotassium aci-dinitroacetate,



Ethyl Dinitroacetate.—The free pseudo acid ester was obtained from

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its potassium salt as follows: 6.2 grams of the salt were powdered and suspended in 100 cc. of water and 10 cc. of ether. The theoretical amount of normal sulfuric acid was slowly dropped into it while it was agitated and kept below 0°. The ethereal solution containing the acid ester was washed with water, sodium carbonate, and again with water, to remove sulfuric acid, and dried over calcium chloride. The ether was evaporated in a vacuum desiccator and a limpid, nearly colorless oil remained. It smelled like willow and when treated with an alcoholic potassium hydroxide solution regenerates the original potassium salt from which it was made, m. p. 196–197°.

The purified oil stains the skin and nails yellow like strong nitric acid. While it is itself practically *colorless* and scarcely soluble in water, one drop of it will impart to several liters of water a decided *yellowish green* color. It slowly decomposes in the sunlight, giving off red oxides of nitrogen and nitric oxide. The free colorless acid ester thus made appears to be the leuco form of the pseudo acid, or its "aci form," which is slowly molecularly rearranged into one or more of the five chromo forms when acted on by water, but much more rapidly and intensely if a little alkali is present (see p. 965).

Salts.—When dry ammonia is passed through an ethereal solution of this acid oil an immediate precipitation occurs of a pale yellow ammonium salt. This salt is unstable. It is soluble in water with decomposition. It dissociates, giving ammonia gas, when boiled in absolute alcohol. By quick solution and cooling, the melting point was raised to 168–169°. The analysis showed it to be impure, however. When placed in a desiccator over caustic potash it slowly dissociates, and coats the sticks of alkali with a yellow film.

A beautiful silver salt may be obtained in yellowish green hexagonal plates by precipitating a concentrated solution of the potassium salt with a concentrated solution of silver nitrate. This silver salt is unstable and is reduced to metallic silver when heated or allowed to stand in the light for some time, or when its aqueous solution is warmed. The crystals melt around 160°.

Beautiful yellow crystallin salts were also formed with ethyl dinitroacetate and aniline, as well as hydrazine.

Potassium Ethyl Nitromalonate.—This potassium salt is contained in the crude potassium salts above mentioned and was obtained by evaporating the aqueous mother liquor from the potassium ethyl dinitroacetate (p. 967) to one-half volume. The crystals thus separated were filtered, washed with alcohol, and further purified by recrystallization from 95 per cent. alcohol. A constant melting point of 145–146° was obtained, but an analysis showed the salt to be impure. Seven grams of this salt were recrystallized four times from absolute alcohol. Three grams were thus

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obtained which melted at 154°. It was dried in a vacuum over sulfuric acid and analyzed.

Calculated for $C_7H_{10}NO_6K$: K, 16.04 ; N, 5.76 ; C, 34.52 ; H, 4.12
Found: K, 16.02, 15.76; N, 6.02, 6.09; C, 34.47, 34.80; H, 4.09, 4.19.

A molecular weight determination on this salt in boiling acetone was made by Mr. Roarke but it did not give a constant value. It indicated some association, increasing with the concentration. The melting point of the salt recovered from the solvent showed that some decomposition had occurred.

	s. Gram.	S. Grams.	*r.*	Mol. wt.	Theory for $C_7H_{10}NO_6K$.
I	0.3143	13.28	0.1340	294.9	205
II	0.5535	13.28	0.1940	358.8	
III	0.7865	13.28	0.2350	420.8	

Potassium ethyl nitromalonate crystallizes in bundles of needles or in beautiful hexagonal prisms of a dark canary-yellow color. Hantzsch[1] has obtained this salt in a pure white form by precipitating a solution of the colorless form of the ammonium salt, with potassium carbonate. It is extremely soluble in water, hot acetone, and hot 95 per cent. alcohol. It is fairly soluble in absolute alcohol, acetone, hot ethyl acetate, and methyl alcohol. It is insoluble in benzene, ligroin, carbon tetrachloride, chloroform, ether, and nearly so in cold ethyl acetate.

Ethyl Nitromalonate from its Potassium Salt.—15 grams of finely powdered potassium ethyl nitromalonate were suspended in 15 cc. of ether and 10 cc. of water. The mixture was chilled in ice water and the theoretic amount, 3.24 grams of sulfuric acid in 50 cc. of water, was slowly dropped into it while the solution was continually shaken to remove the free aci-ester from the aqueous solution as fast as it was formed. The ethereal extract containing the acid oil was thoroughly washed with water, then with a little sodium carbonate solution, which imparts to the nearly colorless ethereal extract a golden yellow color. This coloration was due to the formation of a chromo form of the sodium salt of ethyl aci-nitromalonate. It was again washed with water and dried over anhydrous sodium sulfate for twelve hours. The ether was evaporated in a vacuum desiccator at diminished pressure. The nearly colorless oil which remained was immediately distilled *in vacuo*. The first fraction consisted of 0.5 g. of a colorless oil which boiled from 60°–145° at 33 mm. pressure. The chief product was in the second fraction, 6.5 g. of a colorless oil which boiled at 145–150.5° at the same pressure. The residue consisted of a small amount of yellow oil remaining in the flask.

Fraction two was redistilled and collected in the following fractions, all of which were colorless.

[1] *Ber.*, 40, 1528.

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Fraction No.	Boiling point.	Pressure.	Yield. Gram.
1	140–152°	37–38	1.5
2	152–153°	37–38	2.5
3	154–156.5°	37–38	1.4

A slight residue of yellow oil remained in the flask.

An analysis was made upon the oil of the second fraction with the following results:

Calculated for $O_2N—CH:(CO_2C_2H_5)_2$: C, 40.97 ; H, 5.36; N, 6.82.
Found: C, 41.45, 41.60; H, 5.87; N, 6.81, 6.85.

The product is a clear colorless liquid heavier than water, and possessing a fruit-like odor. While it is itself colorless and insoluble in water as such, a minute quantity of the oil will impart a yellowish green tinge to a large quantity of water. This is due to the molecular rearrangement of the pseudo-acid into a chromo-aci form.[1]

The Ammonium Salt of Ethyl Nitromalonate.—1.17 g. of the ethyl nitromalonate from fraction 2 in the last distillation were dissolved in 20 cc. of ether, and dry ammonia gas passed into it at —10°. An immediate precipitation of a light yellow salt was obtained, which weighed 1 gram. This was filtered off and washed with dry ether and twice recrystallized from hot absolute alcohol. This salt is unstable and ammonia dissociates from it when boiled with alcohol. The recrystallized product consisted of pale yellow, prismatic crystals and melted at 151°. Nitrogen was determined as follows:

$$\text{Calculated for } NH_4O — N = C = (CO_2C_2H_5)_2\text{: N, 12.61. Found: 12.77.}$$

A pure white sample of ammonium ethyl nitromalonate was obtained by recrystallizing the yellow salt, obtained as above, from its solution in cold absolute alcohol, by the addition of two volumes of ether. The colorless crystals are in the form of long needles that melt from 151.5–152°. This process of purification eliminates the decomposition that takes place when it is recrystallized from hot alcohol. The product was analyzed:

$$\text{Calculated for } H_4NO—N=C=(CO_2C_2H_5)_2\text{: N, 12.61. Found: 12.80.}$$

The ammonium salt decomposed when allowed to stand over sulfuric acid in a vacuum desiccator. The pure white salt dissolves in absolute alcohol or in water, to form a *yellow* solution. The color change is here due to a molecular rearrangement of the colorless salt to one of the isomeric chromo forms. The properties of the acid oil and its salts are here shown to be such as to prove their identity with ethyl nitromalonate and its salts.[2]

[1] Hantzsch, *Ber.*, 40, 1533.

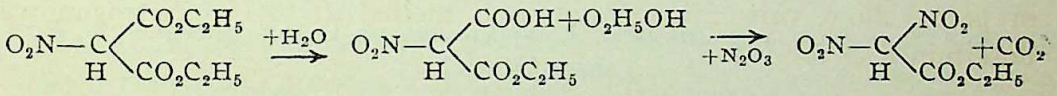
[2] *Ibid.*, 40, 1528; Wohl, *Compt. rend.*, 132, 1052; Franchimont and Klobbie, *Rec. trav. chim.*, 8, 283.

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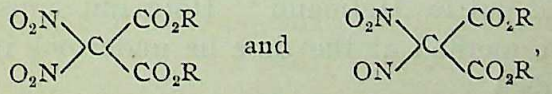
Action of Red Oxides of Nitrogen on Ethyl Nitromalonate.—The red oxides of nitrogen prepared as described above were dried over phosphorus pentoxide and passed into 1.6 g. of ethyl nitromalonate at a temperature of —20°. The ethyl nitromalonate became green; the temperature rose rapidly but it was cooled below 0°. After a large excess of the gas had been condensed in the liquid it was packed in ice for twenty-four hours. The excess of oxides of nitrogen was removed by a current of dry air. The remaining liquid was distilled in a vacuum and passed over clear and colorless at 152° to 154° at 32 mm. This distillate gave a yellow potassium salt which proved to be potassium ethyl nitromalonate. The boiling point and the potassium salt identify this oil as unchanged ethyl nitromalonate. The red oxides of nitrogen when *thoroughly dry* do not, therefore, react with ethyl nitromalonate.

When ethyl malonate is treated with the red oxides of nitrogen to produce the mesoxalic ester, the crude acid oil, which has been the subject of this study, occurs as a by-product. We have frequently noticed when these oils are distilled that the yield of ethyl dinitroacetate is increased at the expense of the ethyl nitromalonate. This shows that under the conditions of the distillation, where water and N_2O_3 are present, ethyl nitromalonate is half saponified, and one carboxyl group is replaced by the NO_2 radical, yielding ethyl dinitroacetate.[1]



We have also noticed that the ethyl nitromalonate largely disappears when the mixture of ethyl malonate, saturated with the red gases, warms up and a violent reaction causes it to "blow off" as frequently happens if not kept well packed in ice for the first ten of twelve hours after saturation.

When dry ammonia gas is passed into the crude oil dissolved in ether the salts of ethyl nitromalonate and ethyl dinitroacetate are first precipitated. At this point the ethereal filtrate should contain any *neutral* nitrogenous esters. An excess of ammonia added suddenly produced a deeper yellow color and soon an unstable red oil separated out. It is from such neutral esters as



which may be left in the ether at this point, that one might expect the production of oxomalonates, $O=C=(CO_2R)_2$, by elimination of the nitro, or nitroso groups in the presence of oxygen during the process of vacuum distillation. The presence of much free nitrogen gas, which was mentioned above as a product of the distillation of these crude oils, appears

[1] See Bouveault and Wahl, *Compt. rend.*, 136, 159.

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to be evidence of the presence of diazomalonic ester, which, with free oxygen, would give nitrogen gas and oxomalonates.

$$\begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!C=(CO_2R)_2 \xrightarrow{+O} N_2 + OC=(CO_2R)_2.$$

Diazomalonic ester has long been sought but without success. Our time was insufficient to investigate these neutral nitrogenous esters.

Mr. Roarke found that the ethereal filtrate, from the crude ammonium salts above mentioned, contains a substance which was obtained by the evaporation of the ether to dryness, and recrystallization of the yellow residue, from benzene-ligroin, and from carbon tetrachloride. The substance was obtained as flat, colorless needles, highly refractive, flexible and greasy to the touch. It melted at 50°, to a yellow liquid. The analysis follows:

C, 41.29, 41.35; H, 8.05, 8.60; N, 16.04, 16.14.

This same product was obtained, by distilling the "crude oils" washed with water, and was found in the fraction of b. p. 97° at 32–34 mm. (uncor.). It is easily soluble in ether, alcohol, acetone, carbon tetrachloride, chloroform, and fairly soluble in benzene and ligroin. It has not been further studied.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY, WORCESTER, MASS.]

THE PREPARATION OF ACETAMIDE.

BY M. A. ROSANOFF, LOUISE GULICK, AND HERBERT K. LARKIN.

Received March 10, 1911.

Methods Used Hitherto.—Acetamide has long been prepared by the action of aqueous ammonia upon ethyl acetate, as originally proposed by Dumas, Malaguti and Leblanc.[1] The reaction mixture has no effect upon iron, and so the process can be carried out on a considerable scale in iron autoclaves.

The preparation of amides from the ammonium salts of the corresponding acids was first introduced by Dumas.[2] The details of this method, as now generally employed for the preparation of acetamide on a laboratory scale, were worked out by Hofmann.[3] Hofmann sums up the condition of the preparative method at the time he undertook its amelioration, in the following words:

"If, however, the preparation of amides hy treating esters with ammonia leaves much to be desired, the yields obtained by the distillation of ammonium salts are even less satisfactory. Experiments on the prepara-

[1] *Comptes rendus*, 25, 657 (1847).
[2] *Ann. chim. phys.*, [2] 44, 142, (1830).
[3] *Ber.*, 15, 977 (1882).

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tion of acetamide by this method have been published by Kündig,[1] who obtained, in the most favorable case, using glacial acetic acid saturated with ammonia gas, something over 25 per cent. of the theoretical yield. In all these distillations streams of ammonia escape at first, which naturally reduces the yield of amide. Petersen,[2] who, at Bunsen's suggestion, modified the experiment by distilling a mixture of equivalent quantities of fused sodium acetate and sal ammoniac, states that acetamide may thus be easily and advantageously prepared, but says nothing concerning the percentage yield. When this experiment was repeated, perfectly pure acetamide was obtained directly, but in this case, too, a large quantity of ammonia was lost and the final yield of acetamide amounted to only 20 per cent. of theory."

Hofmann's method, as given in its optimum form by Gattermann,[3] consists in neutralizing 75 grams of acetic acid with ammonium carbonate and heating in sealed tubes for five hours at 225°. The reaction product is subjected to fractional distillation; the fraction passing over between 180° and 230° is collected separately and on solidification pressed out on a drying-plate. The pressed-out crystals are redistilled, yielding about *40 grams* of almost pure acetamide.

This operation, however, cannot be carried out on a large scale. We quote from Hofmann[4]: "Unfortunately, this operation cannot be carried out, like the treatment of esters with ammonia, in iron autoclaves, as these are strongly attacked. Acetamide will, therefore, be best prepared in the future, as heretofore, by treating the ester with ammonia at ordinary temperatures."

One or two modifications of the Hofmann method have been proposed since 1882. Thus, Schultze[5] warms ammonium acetate with acetic anhydride, using no less than 130 grams of anhydride to 100 grams of the acetate. This, however, is not only costly, but unquestionably yields much diacetamide together with acetamide. Keller[6] distils ammonium acetate in a current of ammonia. We have tried out this method, but with no satisfactory results: unless one carries out a great many redistillations, which is disproportionately laborious, the yield is very small (generally about 12 per cent. of the theory).

New Method.—Hofmann's method has two disadvantages: first, the acetate must be heated in sealed vessels; secondly, iron vessels cannot be employed.

[1] *Ann.*, 105, 277 (1858).
[2] *Ibid.*, 107, 331 (1858).
[3] "The Practical Methods of Organic Chemistry," trans. by Schober (New York, 1907).
[4] *Loc. cit.*, p. 981.
[5] *J. prakt. Chem.*, 27, 512 (1883).
[6] *Ibid.*, 31, 364 (1885).

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From the viewpoint of chemical statics, there is very little advantage in raising the temperature to 220°. According to Menschutkin,[1] the maximum percentages of acetamide formed at different temperatures are as follows:

Temperature.	Maximum per cent. acetamide formed.	Temperature.	Maximum per cent. acetamide formed.
125.0°	75.1	182.5°	82.8
140.0	78.2	212.5	84.0
155.0	81.5		

Obviously, almost as much acetamide could be obtained at 140° as at 220°. The reason that the higher temperature is generally employed is that at lower temperatures the reaction is impracticably slow.

This suggested the possibility of rendering the old method simple and convenient by employing *a suitable catalytic agent.*

The most appropriate catalyst, apparently, was suggested by the following simple considerations. From the fact that the hydrolysis of amides is catalyzed by acids, the inference was drawn that acids would also hasten the opposit reaction, *i. e.*, amide formation. Mineral acids could not be used, as they would take up the ammonia from the ammonium acetate. Organic acids generally would yield their own amides in addition to acetamide. *Acetic acid alone could do no harm and might be confidently expected to promote the reaction catalytically.*

Theoretically it was also clear that, by increasing the volume of the reacting mixtures, the acid catalyzer would improve the yield, since the reaction involves the formation of two molecules (amide and water) from a single molecule (ammonium acetate). This might be expected to counterbalance the slight diminution of yield produced by the temperature lowering.

Experiment soon showed that in the presence of an excess of acetic acid the amide formation really took place with considerable velocity in open vessels. It remained to determin the essential details of the preparation, and this required a large number of trials. The following directions will be found to yield satisfactory results.

First, good dry ammonium acetate is prepared by neutralizing glacial acetic acid with pulverized ammonium carbonate at about 50°, allowing to cool, draining off the crystals, and pressing them out twice or three times with filter paper. The product so obtained contains very nearly 98 per cent. of the pure salt.[2]

100 grams of this ammonium acetate (corresponding to 75 grams of acetic acid) and 113 grams glacial acetic acid (ratio: 1 mol. acetate

[1] *J. prakt. Chem.*, 29, 445 (1884).

[2] The use of ammonium acetate freed from water is best for the obvious reason that water promotes hydrolysis of the amide and hence necessarily diminishes the yield. Commercial ammonium acetate contains more of less free acid and is unreliable, unless neutralized and pressed out afresh.

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1.5 mols. acid) are boiled in a one-liter flask with reflux condenser for 5 hours. The product is rapidly distilled over with minimum loss[1] and subjected to fractionation (again out of a 1-liter flask) with the aid of a two-bulb Wurtz stillhead. *This operation should be carried out as slowly as possible.* Three fractions are collected separately: (1) the fraction passing over below 180°; (2) the fraction passing over between 180° and 213°; (3) the fraction passing over above 213°. During the distilling of fraction 3 the stillhead is unnecessary. The second fraction (180°-213°) is slowly redistilled with the Wurtz stillhead, and the portion passing over above 213° is added to fraction 3, the remainder being added to fraction 1. The original product is thus divided into a low-boiling and a high-boiling fraction. The former may again be neutralized with ammonium carbonate and the resulting salt used for a new preparation. The high-boiling fraction, on thorough solidification, is twice pressed out with filter paper. The dry crystals (practically pure acetamide) weigh *over 60 grams*, or 20 grams more than the product obtained by the use of sealed tubes according to the Hofmann-Gattermann directions. The yield is, however, slightly variable, depending on the quality of the ammonium acetate used and especially on the care with which the fractionation is carried out.[2]

It is obvious that the above directions permit of transforming ammonium acetate into acetamide on as large a scale as may be desired, and should lead to a considerable reduction of the present price of acetamide.

In order to make certain that the low temperature employed did not after all materially diminish the yield, some experiments were carried out on the following plan: 100 grams of our fairly dry ammonium acetate and 113 grams of acetic acid were heated for 3 hours (experiments have shown that even 2 hours would have sufficed) at 225° in sealed tubes. The product was subjected to fractional distillation as described above. The yield was about 56 grams. There is, certainly, no advantage in using sealed tubes.

Our product boils at 214–216°, which shows it to be nearly pure acetamide.

CLARK UNIVERSITY, WORCESTER, MASS.

[1] This distillation materially improves the yield.

[2] In two consecutive preparations carefully carried out in this laboratory by Mr. H. R. Godfrey, the yield was, respectively, 62 and 63.5 grams. At the suggestion of Professor William A. Noyes, Mr. Godfrey was also requested to try the preparation of acetamide from ammonia and an excess of acetic acid directly, without isolating the ammonium acetate. Dry ammonia gas was introduced into 188 grams Kahlbaum's glacial acetic acid (= 75 grams + 113 grams excess, as above) until the increase in weight amounted to 21.3 grams. This was changed to acetamide according to our directions. Two such consecutive trials yielded, respectively, 63.3 grams and 62.2 grams acetamide. The simplification will be valuable when only one preparation is to be carried out.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

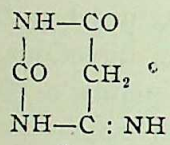
RESEARCHES ON PYRIMIDINES: THIOCYTOSINE-5-CARBOXYLIC ACID.

[FIFTY-SECOND PAPER.]

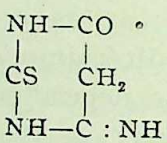
BY TREAT B. JOHNSON AND JOSEPH A. AMBLER.

Received April 12, 1911.

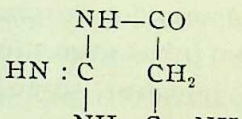
Ethyl cyanoacetate, $CNCH_2COOC_2H_5$, condenses with thiourea and guanidine[1] in the presence of alcohol and sodium ethylate, and cyanoacetic acid with urea in presence of phosphorus oxychloride, giving the pyrimidines—4-iminobarbituric I, 2-thio-4-iminobarbituric II, and 2,4-diiminobarbituric acids III. These iminopyrimidines undergo hydrolysis easily with dilute acids, giving ammonia and the same pyrimidines as are obtained by condensation of diethyl malonate with urea, thiourea, and guanidine, *viz.*: barbituric IV, thiobarbituric V, and 2-iminobarbituric acids VI:[2]



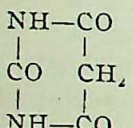
I.



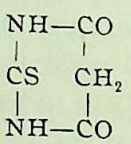
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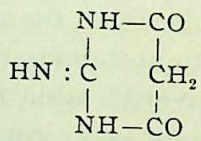
III.



IV.



V.



VI.

Notwithstanding the reactivity of these two esters towards urea, thiourea and guanidine, attempts to obtain mercaptopyrimidines by condensing them with the simple pseudothioureas have been unsuccessful. Wheeler[3] examined the behavior of the strongly acid esters—ethyl acetylcyanoacetate[4] VII, triethyl oxalomalonate[5] VIII, and diethyl oxaloacetate[6] IX—towards pseudoethylthiourea and observed, in every case, that the esters did not react to give pyrimidines but formed stable addition products or salts with the pseudourea. On the other hand, Johnson[7] observed that the higher homolog of diethyl oxalacetate or diethyl oxalopropionate,[8] X, condenses smoothly with pseudoethylthiourea, giving 2-ethylmercapto-4-carbethoxy-5-methyl-6-oxypyrimidine:

[1] Traube, *Ber.*, 33, 1371, 3035; *Ann.*, 331, 64.
[2] Michael, *J. prakt. Chem.*, [2] 35, 456; 49, 36; Traube, *Ber.*, 26, 2553.
[3] *Am. Chem. J.*, 38, 358.
[4] Haller, *Ann. chim. phys.*, [6] 17, 207.
[5] Bouveault, *Bull. soc. chim.*, [3] 19, 78.
[6] Wislicenus, *Ann.*, 246, 317.
[7] *J. Biol. Chem.*, 3, 299.
[8] Wislicenus and Kiesewetter, *Ber.*, 31, 194.

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$CH_3COCH(CN)COOC_2H_5$ VII. $C_2H_5OOCCOCH(COOC_2H_5)_2$ VIII.

$C_2H_5OOCCOCH_2COOC_2H_5$ IX. $C_2H_5OOCOCH(CH_3)COOC_2H_5$ X.

Although diethyl malonate and ethyl cyanoacetate do not condense with pseudothioureas, on the other hand their corresponding ethoxymethylene derivatives, *viz.*: diethyl ethoxymethylenemalonate,[1] XI, and ethyl α-cyano-β-ethoxyacrylate,[2] XII, react smoothly, giving pyrimidines:

$C_2H_5OCH : C(COOC_2H_5)_2$ XI. $C_2H_5OCH : C(CN)COOC_2H_5$ XII.

Wheeler, Johnson and Johns, for example, condensed the malonate, XI, with pseudoethylthiourea and obtained 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine.

Johnson[3] later investigated the action of ethyl α-cyano-β-ethoxyacrylate, XII, on pseudoethylthiourea and made the interesting observation that this ester reacts, in two ways, with the pseudourea, giving a mixture of 2-ethylmercapto-5-cyano-6-oxypyrimidine, XIV, and 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine, XV. The formation of the latter pyrimidine was analogous to that of 2-thio-4-iminobarbituric acid from thiourea and ethyl cyanoacetate.

In continuing our study of the reactivity of ethyl α-cyano-β-ethoxyacrylate, XII, it seemed of interest to examin the behavior of this ester towards thiourea. We now find that it reacts with thiourea in a manner analogous to ethyl cyanoacetate, giving an aminopyrimidine. In fact, it condenses, apparently, in one manner only, giving an excellent yield of 2-thio-4-carbethoxy-6-aminopyrimidine, XIII. We obtained no evidence of the formation of 2-thio-5-cyano-6-oxypyrimidine, XVI. The reaction is expressed by the following equation:

$$\begin{array}{l} NH_2 \\ | \\ CS \\ | \\ NH_2 \end{array} + \begin{array}{l} CN \\ | \\ C \cdot COOC_2H_5 \\ \| \\ CHOC_2H_5 \end{array} = \begin{array}{l} N{=}{=}C \cdot NH_2 \\ | \quad | \\ CS \quad C \cdot COOC_2H_5 \\ | \quad \| \\ NH{-}CH \end{array} + C_2H_5OH$$

XIII.

2-Thio-5-carbethoxy-6-aminopyrimidine, XIII, is converted quantitatively into thiocytosine-5-carboxylic acid, XVIII, by saponification with alkali. This pyrimidine crystallizes from water with one molecule of water while the corresponding cytosine acid[4] separates from water in an anhydrous condition. Especially interesting was the behavior of the

[1] Claisen, *Ann.*, 297, 75.

[2] De Bollemont, *Compt. rend.*, 128, 1338; 129, 5. *Bull. soc. chim.*, [3] 25, 18, 28, 39.

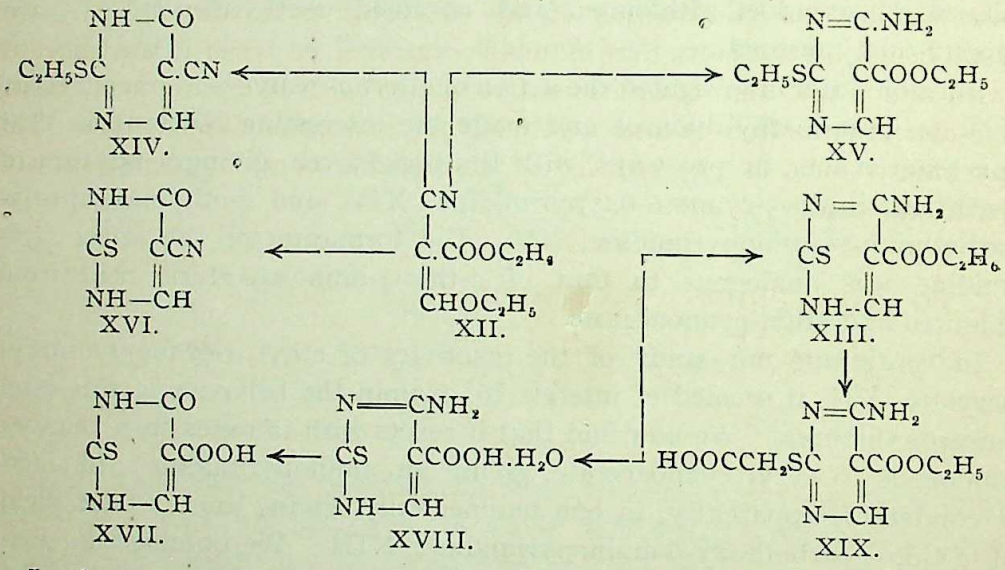
[3] *Am. Chem. J.*, 42, 506.

[4] Wheeler and Johns, *Am. Chem. J.*, 38, 599.

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thiopyrimidine, XVIII, on hydrolysis. Wheeler and Johns[1] observed that the corresponding cytosine derivative was decomposed by heating with 20 per cent. sulfuric acid, giving uracil-5-carboxylic acid. We now find that the sulfur pyrimidine behaves in a similar manner and is converted, quantitatively, under the same conditions, into 2-thio-6-oxypyrimidine-5-carboxylic acid, XVII. It is interesting to note here the firmness with which the sulfur is bound in this pyrimidine. An attempt also to desulfurize 2-thio-5-carbethoxy-6-aminopyrimidine, XIII, by digestion, in aqueous solution, with chloroacetic acid[2] was unsuccessful. They reacted, giving a stable mercaptopyrimidine, *viz.*: 5-carbethoxy-6-aminopyrimidine-2-thioglycolic acid, XIX. These various transformations are represented by the following structural formulas:



In the course of work on thymine compounds now in progress in this laboratory, it was desirable to determin whether thymylamine, XXI, could be obtained from 2,6-dioxypyrimidine-5-acetamide,[3] XX, by the application of the Hofmann rearrangement. Wheeler and Johns[4] have previously attempted to apply this reaction in the pyrimidine series and used in their experiments 2-ethylmercapto-6-aminopyrimidine-5-carboxamide. They observed, however, that no Hofmann rearrangement took place with this amide by treatment with bromine and alkali, and showed that the bromine did not attack the amide group, as might be expected, but added apparently to the double bond in the 4,5-positions, giving a hexahydropyrimidine. When their addition product was treated with alkali it was converted into cytosine-5-carboxamide, 2-ethylmer-

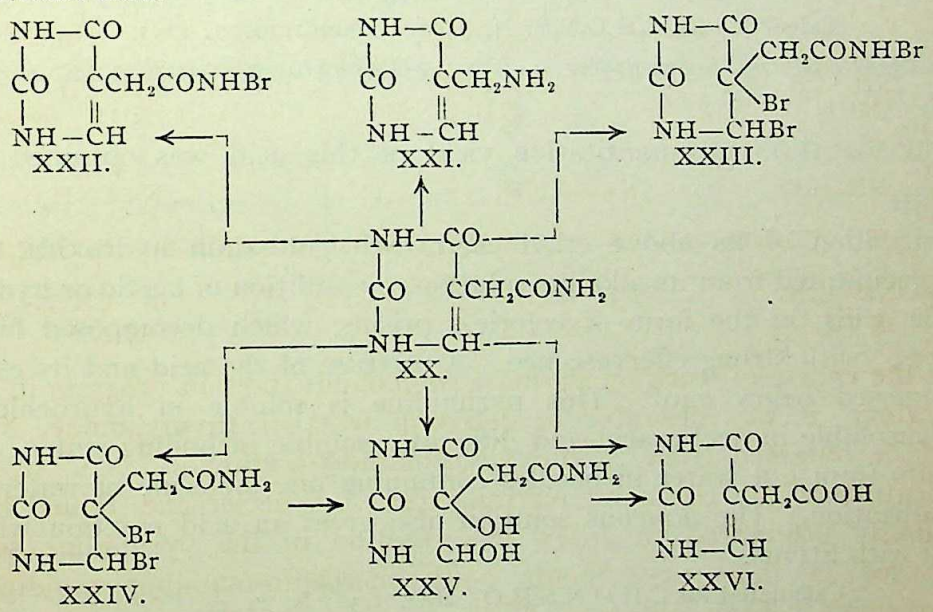
[1] *Loc. cit.*
[2] Wheeler and Liddle, *Am. Chem. J.*, 40, 547.
[3] Johnson, THIS JOURNAL, 33, 745, 758.
[4] *Am. Chem. J.*, 40, 293.

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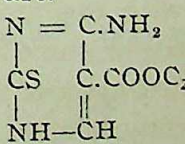
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capto-6-aminopyrimidine or cytosine-5-carboxylic acid, depending on the conditions employed.

We now find that 2,6-dioxypyrimidine-5-acetamide, XX, reacts with bromine in a manner similar to 2-ethylmercapto-6-aminopyrimidine-5-carboxamide and adds the halogen at the double bond of the pyrimidine ring, giving 2,6-dioxy-4,5-dibromohexahydropyrimidine-5-acetamide, XXIV. We obtained no evidence of the formation of bromoamides having the constitutions represented by formulas XXII and XXIII. When the dibromide, XXIV, was warmed gently with alkali it was transformed into a substance having the composition and properties of 2,6-dioxy-4,5-dihydroxyhexahydropyrimidine-5-acetamide, XXV. This transformation, however, was not smooth and the yield of the hexahydro compound was small. The constitution of this dihydroxypyrimidine, XXV, was established by the facts that ammonia was evolved when it was digested with alkali, and that it underwent reduction with hydriodic acid, giving 2,6-dioxypyrimidine-5-acetic acid,[1] XXVI, and ammonium iodide. This pyrimidine acid is not reduced at the double bond by digestion with hydriodic acid.



Experimental Part.

2-Thio-5-carbethoxy-6-aminopyrimidine,  — This pyrimidine was apparently the only compound formed by condensation of thiourea with ethyl α-cyano-β-ethoxyacrylate.[2] Ten grams of the acrylate (1 mol.) and 6.0 grams of thiourea (1.3 mols.) were dissolved in 50 cc.

[1] Johnson and Speh, *Am. Chem. J.*, 38, 602.

[2] *Loc. cit*

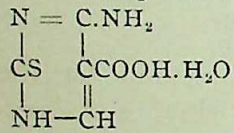
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of absolute alcohol, containing a molecular proportion of sodium, and the solution digested on the steam bath. The alcohol assumed a red color and the pyrimidine began to separate within a few minutes after heating. After heating about 6 hours to complete the reaction, the alcohol was then cooled and the undissolved pyrimidine separated by filtration. By concentration of the filtrate more of the compound was obtained. This pyrimidine is very difficultly soluble in water and insoluble in cold alcohol. It is somewhat soluble in boiling, glacial acetic acid and crystallizes from this solvent or hot water in needles. It darkens at about 250°, when heated in a capillary tube, and then decomposes from 260–265° according to the rate of heating. The pyrimidine is soluble in cold alkali and is precipitated unaltered by addition of mineral acids. It is a weak base and its salts easily dissociate in aqueous solution. The hydrochloride separates from a hot solution of 25 per cent. hydrochloric acid in colorless prisms, which decompose at 209–211° with violent effervescence. When dissolved in water the salt is decomposed and the pyrimidine separates in needles melting at 260–265°. The yield of purified pyrimidine was 8.4 grams. Analysis (Kjeldahl):

Calculated for $C_7H_9O_2N_3S$: N, 21.10. Found: 20.77, 21.1.

2-Thio-5-carboxyl-6-aminopyrimidine (2-Thiocytosine-5-carboxylic Acid),



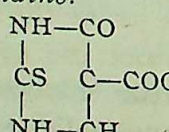
$N=C.NH_2$
$CS\quad CCOOH.H_2O$
$NH-CH$

—A quantitative yield of this acid was obtained by saponification of its above ethyl ester with potassium hydroxide. It was precipitated from its alkaline solution, by addition of acetic or hydrochloric acids, in the form of colorless prisms, which decomposed from 253–263° with strong effervescence. A mixture of the acid and its ester decomposed below 240°. This pyrimidine is soluble in hydrochloric acid, insoluble in acetic acid and difficultly soluble in boiling water. It deposits from hot water in needles containing one molecule of water of crystallization. The aqueous solution also gives an acid reaction when tested with litmus.

Calculated for $C_5H_5O_2N_3S.H_2O$: H_2O, 9.52; N, 22.22.
Found: H_2O, 9.32; N, 22.3, 21.8.

Action of 20 Per cent. Sulfuric Acid on 2-Thio-5-carboxyl-6-amino-pyrimidine.

2-Thio-5-carboxyl-6-oxypyrimidine,



$NH-CO$
$CS\quad C-COOH$
$NH-CH$

—One gram of the hydrous amino acid was dissolved in 40 cc. of 20 per cent. sulfuric acid and the solution boiled for 20 hours. After cooling, the above pyrimidine separated as a heavy, yellow powder. It was purified for

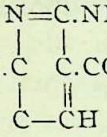
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analysis by recrystallization from hot water and separated, on cooling, in granular crystals which melted with decomposition at 246–247°. It gave a strong test for sulfur and the yield of purified material was 0.42 gram. Analysis (Kjeldahl):

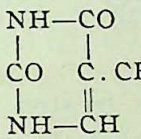
Calculated for $C_5H_4O_3N_2S$: N, 16.39.
Found: N, 16.35, 16.47.

5-Carbethoxy-6-aminopyrimidine-2-thioglycolic Acid,

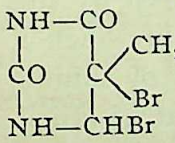


$HOOC.CH_2S.C\ \ C.COOC_2H_5$.—This pyrimidine was obtained in an attempt to desulfurize 2-thio-5-carbethoxy-6-aminopyrimidine by digestion with chloroacetic acid in aqueous solution. It was difficultly soluble in hot water and separated as a light brown powder, which decomposed at 174–177° with effervescence. Analysis (Kjeldahl):

Calculated for $C_7H_7O_4N_3S$: N, 18.34.
Calculated for $C_9H_{11}O_4N_3S$: N, 16.35.
Found: N, 16.9.

2,6-Dioxypyrimidine-5-acetamide,  . —This pyrimidine, which has been described in a previous paper,[1] was prepared for the following experiments by heating the corresponding ethyl 2,6-dioxypyrimidine-5-acetate with aqueous ammonia. An attempt to prepare the amide by heating the ammonium salt of 2,6-dioxypyrimidine-5-acetic acid was unsuccessful.

2,6-Dioxy-4,5-dibromohexahydropyrimidine-5-acetamide,



. —Eight grams of potassium hydroxide (8 mols.) were dissolved in 50 cc. of cold water and the solution divided into two portions of 37.5 cc. and 12.5 cc., respectively. In the first portion (37.5 cc.) were dissolved 5.6 grams of bromine (2 mols.), and 3.0 grams of finely pulverized 2,6-dioxypyrimidine-5-acetamide were then slowly added while keeping the temperature of the solution below 20°. After complete solution of the amide the second portion of potassium hydroxide (12.5 cc.) was added and the solution finally heated at 85° for half an hour. There was only a slight evolution of ammonia, under these conditions, and a dark-red-colored solution was obtained. After cooling and filtering from a small amount of amorphous precipitate the solution was acidified with glacial acetic acid, filtered, and finally evaporated to

[1] Johnson, *Loc. cit.*

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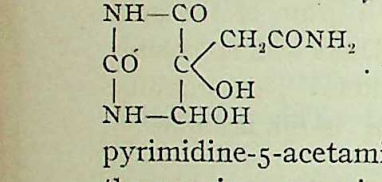
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dryness. We obtained a dark colored residue, which was again dissolved in water and the solution decolorized with bone-coal. On evaporation to dryness a yellow crystallin substance, mixed with sodium acetate, was obtained. By extraction of this material, however, with absolute alcohol, the dibromohexahydropyrimidine was obtained as a light yellow powder, which was very soluble in water. It was identified by means of its picrate which crystallized from water in beautiful yellow needles. This compound decomposed when heated above 280° and gave a strong test for bromine. Analysis (Kjeldahl):

Calculated for $C_6H_7O_3N_3Br_2.C_6H_3O_7N_3$: N, 15.10.
Found: 15.4.

When the material above, insoluble in alcohol, was digested with alkali ammonia was evolved and a clear solution obtained. After cooling and acidifying with hydrochloric acid a crystallin substance separated which was identified as 2,6-dioxypyrimidine-5-acetic acid.

2,6-Dioxy-4,5-dihydroxyhexahydropyrimidine-5-acetamide,



. — In this experiment 2.75 grams of 2,6-dioxypyrimidine-5-acetamide were treated with bromine (5.13 grams) as in the previous experiment, except that 10 molecular proportions of potassium hydroxide were used in the reaction instead of eight. After allowing the solution to stand a few minutes and then warming to 85° it was cooled and acidified with hydrochloric acid. The solution was then evaporated to dryness when an orange-colored powder, mixed with potassium chloride, was obtained, which was digested with alcohol. About 1.2 grams of a yellow substance were dissolved by this solvent. It was purified by crystallization from hot water, in which it was quite soluble, and separated on cooling in aggregates of minute lemon-yellow prisms, resembling in crystallin appearance that of uracil. They decomposed at about 270–280°, giving a tar, and then effervesced when heated to about 285–286°. The pyrimidine was soluble in alkali, and ammonia was evolved when the alkaline solution was heated. It did not give a test for halogens. The low analysis for nitrogen was probably due to the presence of a small amount of 2,6-dioxypyrimidine-5-acetic acid as impurity. Analysis (Kjeldahl):

Calculated for $C_5H_7O_2N_3$: N, 29.78.
Calculated for $C_6H_9O_5N_3$: N, 20.6.
Found: N, 19.8.

Reduction of 2,6-Dioxy-4,5-dihydroxyhexahydropyrimidine-5-acetamide to 2,6-Dioxypyrimidine-5-acetic Acid.—About 0.8 gram of the above hexahydropyrimidine was dissolved in 15 cc. of colorless hydriodic acid and

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the solution boiled for 2 hours. Iodine was evolved immediately and deposited on the surface of the condensing tube. After cooling and diluting with water, the iodine was reduced by addition of sulphur dioxide solution, when we obtained a clear pale yellow solution. This was finally concentrated, decolorized with charcoal, and cooled. Beautiful, colorless prisms deposited, which did not melt below 300°. The compound was identified as 2,6-dioxypyrimidine-5-acetic acid. The yield was nearly quantitative. A mixture of this and thymine melted below 260°. The compound contained no halogen, was soluble in alkali, and was precipitated from its alkaline solution by addition of acids. When the above mother liquor (HI solution) was digested with an excess of sodium hydroxide, ammonia was evolved, showing the presence of ammonium iodide in the solution. Analysis (Kjeldahl):

Calculated for $C_6H_6O_4N_2$: N, 16.47.
Found: N, 16.44.

2,6-Dioxypyrimidine is not reduced at the double bond in the 4,5-positions by the action of hydriodic acid. One-half a gram of the acid was recovered unaltered after digestion for 3 hours. There was no coloration of the acid, due to the formation of any free iodine. This stability of the unsaturated ring, in presence of hydriodic acid, is remarkable.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

METHYL PHENYLIMINOMALONATE AND ITS REACTIONS.

BY RICHARD SYDNEY CURTISS AND F. GRACE C. SPENCER.

Received April 26, 1911.

We have for some time sought a method of making the above-named compound, $C_6H_5N=C(CO_2R)_2$, but without avail. Considered as a dicarboxyl addition product of phenyl isocyanide, $C_6H_5N=C$, or as an analog of phenyl isocyanate, $C_6H_5N=C=O$, containing the negative carbomethoxyl groups in place of oxygen, one might predict its chemical properties and behavior with some degree of accuracy. As Nef[1] and others have so well shown in the case of isocyanides and isocyanates, they possess a great reactivity on the N=C double bond—adding on at this point many compounds having easily dissociable hydrogen atoms. In such cases of addition with isocyanides, RN=C, in which the carbon is bivalent, it is the higher valences of the carbon atom which show the greatest reactivity. They first become saturated, yielding compounds of the isocyanate type, $RN=C=O$ and $RN=C\langle^{H}_{X}$; further addition takes place on the N=C double bond; for instance with ammonia; the phenyl

[1] *Ann.*, 270, 268–335; 280, 291–342; 287, 265–359; and other papers.

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isocyanate, $R—N=CO$, yields carbonic acid derivatives, $RNH.CO.NH_2$, $\begin{matrix} + \\ H—NH_2 \end{matrix}$ ureas. The well-known action of water upon these isocyano compounds results in their hydrolysis and the formation of an amine, and an acid,

$$RN=C+2H_2O \qquad RNH_2+O=C\begin{matrix}H\\OH\end{matrix}.$$

$$RN=CO+2H_2O \qquad RNH_2+\begin{matrix}HO\\HO\end{matrix}\!\!>\!CO$$

The latter reaction proceeds with the formation of one or more less stable intermediate reaction products of the isocyanate with water; for instance one of these reactions yields disubstituted ureas,

$$2R—N=CO+2H_2O \longrightarrow \begin{matrix}RNH\\RNH\end{matrix}\!\!>\!CO+(HO)_2:CO,$$

and the latter may be further hydrolyzed to the final products, an amine and carbonic acid.

As far as we have been able to find, the exact mechanism of the reaction of water with the isocyanates, producing the above compounds, has not been discovered. In the last reaction it is apparent that the R—N radical must dissociate from the carbon of the isocyanate in order to produce the second amine group which is present in the product. Whether or not this dissociation of the nitrogen from carbon precedes, or follows, the addition of the elements of water upon the N=C double bond remains to be proved. The exact mechanism of the hydrolysis of the isocyanides and isocyanates is of much importance, and is discussed here, inasmuch as the study of the phenyliminomalonates and their reactions throws an interesting light upon this point.

In attempting to prepare the esters of phenyliminomalonic acid, $C_6H_5N=C(CO_2H)_2$, we have tried the effect of heat upon ethyl dianilinomalonate in the hope of dissociating one molecule of aniline, but without success.

$$\begin{matrix}C_6H_5N—\\H\\C_6H_5NH\end{matrix}\!\!>\!C(CO_2C_2H_5)_2 \longrightarrow C_5H_5N=C(CO_2C_2H_5)_2+C_6H_5NH_2$$

As we have since learned, the reactivity of the product sought is so great that it could not exist in the presence of aniline, which reverses the reaction completely. This is in marked contrast to the behavior of dianilinoacetic acid, which loses aniline at ordinary temperature.

Ostromisslenskii[1] obtained phenyliminoacetic acid, $C_6H_5N=CH.CO_2H$, from dianilinoacetic acid, $\begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}\!\!>\!CH.CO_2H$, by simply allowing the

[1] *Ber.*, 41, 3029.

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substance to stand in a desiccator, but with better results by heating, alone or in the presence of acetic acid. The product is yellow, reactive at the point of the N=C double bond, and easily polymerizes.

We have, however, produced methyl phenyliminomalonate in nearly theoretical yield and in a pure form by the action of phosphorus pentoxide upon methyl anilinotartronate, $C_6H_5N(H)—C(OH)=(CO_2CH_3)_2$ + $P_2O_5 = C_6H_5N=C=(CO_2CH_3)_2$. The product is a thick greenish-yellow oil, with great reactivity on the N=C double bond, which here acts also as a chromophore group. It reacts vigorously with water, alcohols, dry ammonia, dry hydrochloric acid, amines, and acids, with loss of color, and the formation of substituted anilinomalonates. It polymerizes readily to gums and resins.

Even the moisture of the air rapidly changes the yellow oil to colorless crystallin compounds, methyl dianilinomalonate and methyl dihydroxymalonate. This reaction has been studied quantitatively. Its mechanism is complex and appears to be in perfect analogy with that of water upon phenyl isocyanate producing diphenylurea, as mentioned above.

We have also studied the action of ethyl alcohol upon methyl phenyliminomalonate. It yields a crystallin addition product, methyl anilinoethoxymalonate, $\begin{matrix} C_6H_5NH \\ C_2H_5O \end{matrix}\!\!>\!C=(CO_2CH_3)_2$.

Methyl phenyliminomalonate adds one molecule of aniline at ordinary temperatures and yields methyl dianilinomalonate, $\begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>\!C:(CO_2CH_3)_2$.

This compound we have also made for comparison by the action of aniline upon methyl dihydroxymalonate.

It was formerly observed by one[1] of us that ethyl anilinomalonate was converted into ethyl dianilinomalonate by simply heating the substance, in dry ligroin solution, with freshly precipitated mercuric oxide. The latter is quickly reduced. We have tried the same reaction on methyl anilinomalonate. With this ester the reduction of the mercuric oxide proceeds much more slowly and incompletely, but in like manner yields the substituted diaminomalonate and dihydroxymalonic ester.

The mechanism of this reaction is complex. It is closely related to the production of the same dianilinomalonates when water acts upon phenyliminomalonates as described above on this page.

The mechanism of the formation of diphenylurea, amine, and acid, by the hydrolysis of phenyl isocyanates (p. 986), is no doubt to be ex-

[1] Curtiss, *Am. Chem. J.*, 19, 694.

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plained in a similar manner. These related reactions are the subject of further investigations in this laboratory, with the purpose of determining what unstable intermediate products may be formed, or for a time exist, between the starting point and the production of the stable end products.

The above-mentioned analogies between the addition reactions of methyl phenyliminomalonate and those of phenyl isocyanate is brought out in the following tabulation, in which R′ represents the phenyl radical, and the parentheses enclose the hypothetical addition products which have not yet been separated out.

1	$R'N=CO$	by H_2O →	$(R'NH\diagdown^{HO}\!\!>CO)$ — ⌐
		" ←	$(R'NH)_2CO$ ←— ⌙
	$R'NH_2+(HO)_2CO$		
1′	$R'N=C:(CO_2R)_2$	by H_2O →	$R'NH\diagdown^{HO}\!\!>C=(CO_2R)_2$ ——— ⌐ loss H_2O
		" ←	$(R'NH)_2=C:(CO_2R)_2$ ←— ⌙
	$R'NH_2+(HO)_2C(CO_2R)_2$		
2	$R'N=CO$	by HOR →	$R'NH\diagdown^{RO}\!\!>CO$
2′	$R'N=C:(CO_2R)_2$	" →	$R'NH\diagdown^{RO}\!\!>C:(CO_2R)_2$
3	$R'N=CO$	by NH_3 →	$R'NH\diagdown^{NH_2}\!\!>CO$
3′	$R'N=C(CO_2R)_2$	" →	$R'NH\diagdown^{NH_2}\!\!>C:(CO_2R)_2$? w. cryst. → Polymers.
4	$R'N=CO$	by $R'NH_2$ →	$(R'NH)_2=CO$
4′	$R'N=C(CO_2R)_2$	" →	$(R'NH)_2=C:(CO_2R)_2$
5	$R'N=CO$	by HCl →	$(R'NH\diagdown^{Cl}\!\!>CO)$? → Polymers.
5′	$R'N=C:(CO_2R)_2$	" →	$R'NH\diagdown^{Cl}\!\!>C:(CO_2R)_2$? w. cryst. → Polymers.

The reactions of phenyliminomalonates with water, dry ammonia, and hydrochloric acid gas yield colorless, unstable, intermediate products which quickly pass over into more stable ones.

Experimental.

Methyl Phenyliminomalonate, $C_6H_5N=C(CO_2CH_3)_2$: *The Action of Phosphorus Pentoxide on Methyl Anilinotartronate.*—Ten grams of methyl anilinotartronate[1] were thoroughly mixed with two and five-tenths

[1] Preparation, see Curtiss and Spencer, THIS JOURNAL, 31, 1057.

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grams of phosphorus pentoxide (one mo . = 1.97 grams) and allowed to stand at the room temperature. At the end of two days it was a yellow sticky mass. (Sometimes the reaction begins almost immediately when mixed, and in one case it stood two weeks before any change was noticed.) At the end of six days it had separated into a heavy yellow and a hard yellow-red solid. The oil cannot be purified by vacuum distillation as it decomposes, nor can it be crystallized. A portion of the oil was decanted, and the remainder was dissolved in five times its volume of sodium-dry ether. The solid portion was insoluble in ether. Analysis was made on both the decanted sample and the one which had been extracted with ether, after the ether had been evaporated in a vacuum desiccator, over sulphuric acid.

Calculated for $C_6H_5N=C(COOCH_3)_2$: C, 59.69 ; H, 5.02 ; N, 6.33.
Found: C, 59.98, 60.01; H, 5.00, 4.79; N, 6.10, 6.61.

Methyl Phenyliminomalonate is a thick golden yellow oil, having a sharp biting taste. The presence of the double bond N=C, reacting with the two adjacent carbonyl groups, acts as a chromophore and gives it color, and also makes it an extremely reactive substance. As already mentioned, it combines readily with the moisture of the atmosphere when exposed to the air, adds on the dissociated parts of water, alcohols, acids, ammonia, amines, and other compounds containing easily dissociable hydrogen atoms, and in many ways suggests the great reactivity of the unsaturated isocyano group in the isocyanides, RN = C, and isocyanates, RN = CO.

Action of Aniline on Methyl Phenyliminomalonate.—Three and two tenths grams of methyl phenyliminomalonate were mixed with one and seventy one-hundredths grams of aniline (1 mol.). The temperature rose thirty-five degrees, and the mixture turned to a thick glycerol-like syrup, which quickly changed to a colorless crystallin mass. It was recrystallized several times by dissolving in sodium-dry ether and evaporating the solvent in a vacuum desiccator over sulfuric acid, then filtered and washed with cold ether. Attempts to concentrate the solution on a water bath produced a yellow gummy mass, which it was almost impossible to purify:

Calculated for $(C_6H_5NH)_2C=(COOCH_3)_2$: C, 64.91 ; H, 5.78 ; N, 8.93.
Found: C, 64.94, 65.04; H, 5.99, 5.74; N, 8.73, 9.25.

Methyl dianilinomalonate is a white crystallin substance having a melting point between 124 and 125°. Its crystals appear as hexagonal plates. It is easily soluble in benzene, acetone, and chloroform, fairly soluble in acetic ester, absolute ethyl and methyl alcohols, and slightly soluble in ligroin, and insoluble in water. It becomes electrified when rubbed with a glass rod. These properties identify it with the product

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made by Conrad and Reinbach.[1] We have also prepared this substance by the following method:

The Reaction of Aniline with Methyl Dihydroxymalonate.—Forty-nine grams of methyl dihydroxymalonate were mixed with 5.58 grams of aniline and heated on a water bath for 30 minutes. At 65° the action began, water was formed and deposited on the sides of the flask, and the substance changed to a thick yellow oil When removed from the water bath it was dark in color It was extracted with ether and the dark red solution was washed thoroughly with 10 per cent. hydrochloric acid solution, and then with water to remove the excess of aniline. It was then dried with potassium carbonate and evaporated on a water bath. The crystal product was again recrystallized from dry ether and then melted at 124–125°. Analysis:

Calculated for $(C_6H_5NH)_2=C=(COOCH_3)_2$: C, 64.95; H, 5.78; N, 8.94.
Found: C, 65.13; H, 5.69; N, 9.29.

The properties of this product are identical with those of methyl dianilinomalonate prepared as was described above.

Action of Water on Methyl Phenyliminomalonate.—Two grams of methyl phenyliminomalonate were mixed with one gram of water The water immediately becomes "milky" and the oil turns to a lemon-yellow color and becomes thick and viscid. The substance changes to a hard, dry, nearly colorless crystallin mass when allowed to stand for one day. It was then washed several times with a total of seven cc. of water to remove the methyl mesoxalate which appeared as one of the products of the reaction. The remaining crystals were then dissolved in ether and washed with water. A yield of 1.28 g. of crude crystals was obtained, m. p. 112°. The substance, when purified by recrystallization from ether, weighed 0.9 gram and melted at 124°. It was submitted to analysis with the following results. Analysis:

Calculated for $(C_6H_5NH)_2=C=(COOCH_3)_2$: C, 64.91; H, 5.78; N, 8.93.
Found: C, 65.05; H, 5.61; N, 8.71.

The properties of this substance are identical with those of methyl dianilinomalonate, as given above.

All the water which was used to wash the crystallin product mentioned above was evaporated in a desiccator. 0.9 gram of a colorless crystallin compound was obtained which dissolved readily in alcohol, water, and most organic solvents. It melted at 78°. The analysis follows:

Calculated for $(HO)_2=C=(CO_2CH_3)_2$: C, 36.57; H, 4.92.
Found: C, 36.70; H, 5.49.

The solubilities and chemical properties of this substance were found to be identical with those of methyl dihydroxymalonate.[2]

[1] *Ber.*, 35, 521.

[2] Curtiss and Tafflowski, THIS JOURNAL, 30, 1267.

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So great is the reactivity of the N=C double union in methyl phenyliminomalonate with water, that it absorbs it vigorously from the air, and it is impossible to keep the yellow oil in a state of purity, except in a desiccator over a strong dehydrating agent, or in sealed tubes. Two grams of the oil were exposed to the air for a few days, the yellow color disappeared quite rapidly as water was absorbed, and a solid crystallin mass resulted. Methyl dianilinomalonate and methyl dihydroxymalonate were separated from the product in the manner above described. The compounds were identified as such, both by their analyses and by a study of their chemical and physical properties.

Methyl dianilinomalonate has also been produced in the following interesting manner:

Oxidation of Methyl Anilinomalonate.—The methyl anilinomalonate used was prepared by the action of aniline upon ethyl bromomalonate, in a manner similar to that already described for the corresponding ethyl compound. One gram of methyl anilinomalonate, $C_6H_5NH.HC:(CO_2CH_3)_2$, dissolved in dry ligroin was mixed with 1.08 grams of freshly precipitated mercuric oxide, and the mixture heated on a water bath with a reverse condenser for fifteen hours, moisture of the air being excluded. The reduction of the oxide takes place slowly and incompletely. The grass-green solution was filtered from the mercury and mercuric oxide, and evaporated on the water bath. Crystals formed in hexagonal plates and melted in the impure form at 78°. This is the melting point of methyl dihydroxymalonate. The product was recrystallized five times and then showed a melting point of 124°, and this purified product corresponds in melting point and other properties to ethyl dianilinomalonate. The oxidation goes much more rapidly when the substance is dissolved in xylene and kept at a temperature of 130 to 150°, especially if a little hydrochloric acid is present to act as a catalyzer. The product in this test is apparently a mixture of methyl dihydroxymalonate, and methyl dianilinomalonate, by the same complex reaction which one of us has described for the corresponding ethyl ester.[1]

Action of Ammonia and of Hydrochloric Acid Gas on Methyl Phenyliminomalonate.—When dry ammonia gas is passed into an ethereal solution of methyl phenyliminomalonate, an intense reaction takes place and a white crystallin substance is formed, along with a red gummy product. The former substance is but slightly soluble in ether, and when exposed to the air it becomes gummy and rapidly loses ammonia. The product has not yet been purified. It is very unstable and seems to pass easily into polymerization products.

When dry hydrochloric acid gas is passed into methyl phenylimino-

[1] *Am. Chem. J.*, 19, 694.

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malonate, either in the pure form, or in solution in dry ether, a white crystallin reaction product is formed. This is also very unstable and rapidly liquefies in the air, losing hydrochloric acid, and appears to produce gummy polymerization products. This polymerization of the phenyliminomalonate appears analogous to that of phenyl isocyanate.

The Action of Alcohol on Methyl Phenyliminomalonate.—We have tested the action of methyl and ethyl alcohols, as well as benzyl alcohol, upon this substance. They all react vigorously with the evolution of heat, and loss of color of the iminomalonate, and produce well-defined, crystallin addition products. Mr. J. H. Bornmann has carried out the study of the product produced from ethyl alcohol, and in the following manner:

2.35 grams of methyl phenyliminomalonate were mixed with 0.49 gram (1 mol.) of absolute ethyl alcohol. There was an evolution of heat, a loss of color, and after a few hours the thick oil crystallized in colorless crystals. The substance was washed and recrystallized from alcohol and melted at 88° (uncor.). It is easily soluble in ether, benzene, chloroform and carbon tetrachloride; fairly soluble in alcohol; and slightly soluble in ligroin. While colorless in the pure form it slowly turns yellow when kept in a desiccator over sulphuric acid. This color change is probably due to a loss of alcohol and reproduction of the N=C double bond, which here acts as a chromophore in the phenylimino-malonate:

Calculated for $\begin{matrix} C_6H_5NH \\ C_2H_5O \end{matrix}\!\!>\!C : (CO_2CH_3)_2$: C, 58.42; H, 6.36; N, 5.24.

Found: C, 58.65; H, 6.39; N, 5.17.

URBANA, ILL.

NOTES.

Hippuric Acid as the Cause of the Failure of the Spectroscopic Test for Hemoglobin in Urine.—During the winter of 1910–1911, Passed Assistant Surgeon C. H. Lavinder, of the Division of Pathology and Bacteriology of the Hygienic Laboratory, called my attention to the difficulty he was having in the identification of blood coloring matter in the urine from a case of suspected paroxysmal hemoglobinuria. The urine in question presented an appearance which would lead a clinician to suppose blood coloring matter to be present, and yet, when examined with the spectroscope, no absorption bands such as are produced by hemoglobin and its various derivatives in solution, were to be seen. Later, Dr. Lavinder succeeded in obtaining Teichman's crystals in the usual manner, and thus demonstrated the presence of blood coloring matter in the specimen of urine under examination.

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In endeavoring to find an explanation for the non-appearance of the hemoglobin of other absorption bands in the spectrum of this specimen of urine, Dr. Lavinder introduced some fresh blood into a specimen of human urine known to be free of blood pigments, and noted that while at first the solution gave the characteristic hemoglobin spectrum, the bands gradually became indistinct, and eventually faded out entirely.

It thus appeared that there is present in normal urine some constituent which has the power of destroying hemoglobin, or at least of rendering it inactive spectroscopically. With the view of learning more on this point, and if possible, of determining the constituent of urine responsible for this conduct of the hemoglobin, the writer recently made the following experiments:

Solutions were made, as strong as possible, of uric acid and hippuric acid in distilled water. Owing to the very slight solubility of these acids, the solutions were very dilute. A third solution contained three per cent. of urea—a little more concentrated than this compound would normally be found in urine. Approximately equal amounts, about 0.1 gram, of fresh blood were introduced into 25 cc. portions of each of these solutions and also into distilled water in equal amount. The blood was introduced into the solutions successively as they were taken up, in order that the blood-containing solutions should not be standing while one was being examined. The solutions were then examined by means of a small Schmidt and Haensch direct-vision spectroscope, mounted vertically above a cylindrical absorption cell. In all four solutions, the characteristic spectrum of oxyhemoglobin was at first produced, the bands being very clearly seen. With the distilled water, the uric acid, and the urea solutions, no effect was observed, even after one-half to one hour's standing. With the hippuric acid solution, however, the characteristic spectrum could be seen to be fading even during observation, and at the end of five minutes the absorption bands had entirely disappeared. The series was repeated with exactly similar results. The disappearance of the characteristic hemoglobin spectrum was accompanied by a visible change in the appearance of the solution; immediately after the introduction of the blood, the solution presented the usual pinkish color of a dilute blood solution, but gradually became more and more brownish, until after the bands had entirely disappeared the solution presented a color much like that of a strong solution of ferric alum.

A few drops of the hippuric acid solution added to the 25 cc. of distilled water containing blood, acted more slowly, and finally appeared to cease to act, the absorption bands remaining visible for some time, but much less distinct than at first. In another experiment, the hippuric acid solution was found to be active in the presence of urea, of uric acid, and of both the latter.

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To further test this matter, small portions of fresh blood were added to one per cent. solutions of hydrochloric, sulfuric and nitric acids, ammonium hydroxide and sodium hydroxide. All three acids immediately destroyed the hemoglobin spectrum, the action of the nitric acid being the most rapid. The sodium hydroxide solution also destroyed the spectrum, though not quite so rapidly, while the ammonium hydroxide solution did not appear to weaken the intensity of the absorption bands even after several hours' standing. This is, of course, in accordance with the well known production of hemoglobin-derivatives through the action of acids and caustic alkalis.[1] It would appear that in urine the action is due to the acidity produced by the hippuric acid; solutions, of this acid in water of a concentration equal to that in which it might be expected to occur in urine, are distinctly acid to litmus, while solutions of uric acid of the greatest concentration obtainable at ordinary temperatures react but very feebly acid to litmus. After neutralization of the hippuric acid solution to a distinctly alkaline reaction with sodium hydroxide, the absorption spectrum was still slowly destroyed, probably by the excess of alkali. Neutralization with ammonia and rendering slightly alkaline with the same reagent prevented the destruction of the characteristic spectrum, the spectral appearance remaining constant for about four hours, at the end of which it was as definit as at first.

In all of the above the spectrum observed was that of oxyhemoglobin. No spectroscopic evidence was obtained of the formation under these conditions, in solutions of the concentrations used of the absorption spectra of other forms of hemoglobin, or of its derivatives. The fact that so-called "hemoglobinuria" is usually actually "hematinuria" has frequently been noted, and the case in point seems to be an example. The fa lure of the hematin spectrum may have been due to the adsorption of the hematin by some phosphate or other precipitate.

It is somewhat strange that there is little or nothing on the failure of the spectroscopic test for *hemoglobin* in urine, in either the medical or chemical or chemical literature Most of the textbooks on legal and clinical chemistry recommend the spectroscopic tests for hemoglobin as the most definit and one of the most delicate tests for blood coloring matter, and no question as to its applicability to urine seems to have been raised. Perhaps this is mainly due to the fact that the spectroscope seems to have been employed but very little in testing for blood in urine, preference having usually been given to the chemical (oxygen-carrier) tests and the formation of hemin or other crystals.

It would seem desirable, therefore, that when a specimen of urine is suspected to contain blood-coloring matter, and has to be laid aside for some time before the application of the spectroscopic test for *hemoglobin*

[1] See Neubauer and Vogel, *Analyse des Harns*, 10th Ed., pp. 495, 554.

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it should first be rendered slightly alkaline with ammonia water, in order to prevent the destruction of the hemoglobin, if present, by the acids (mainly hippuric) present in the urine.

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NEW BOOKS.

A Laboratory Manual of Inorganic Chemistry. By EUGENE C. BINGHAM, Ph.D. (Johns Hopkins), Professor of Chemistry, Richmond College, Richmond, Virginia, AND GEORGE F. WHITE, Ph.D. (Johns Hopkins), Associate Professor of Chemistry, Richmond College, Richmond, Virginia. New York: John Wiley and Sons. London: Chapman and Hall, 1911. viii + 147 pp. Price, $1.00 net (4/6 net).

This is a 12mo. volume printed on a stout paper, interleaved with blank pages, and neatly bound in dark blue cloth. The subject matter is divided into three parts: Part I, "Inorganic Preparations" (45 pp.), deals with the preparation and examination of the common gases, and of a few other substances such as bromine, iodine, potassium chlorate and sodium hydroxide. Part II, "Qualitative Analysis" (74 pp.), discusses the dry-way tests, and the wet-way reactions of and analysis for basic and acidic radicals, with the group separations. For the method of separating the metals of the iron and zinc groups the authors "are largely indebted to Messrs Noyes, Bray and Spear." Part III, "Quantitative Analysis" (11 pp.), gives detailed directions for half a dozen quantitative experiments illustrating the fundamental laws. These experiments, it is stated, may be introduced at the discretion of the instructor during the early part of the course.

The instructions throughout are admirably lucid and "have been made full, so that no good excuse may be offered for slovenly work." In Part I, the student is required to answer questions frequently but not perpetually. Part II abounds in formulas and equations and is thus not merely a set of laboratory directions to accompany a reference work, but is itself largely informative, stating what happens rather than enquiring this of the student. References to other text-books are, indeed, not frequent. The only general inorganic text cited in the list of chemical reference literature on p. 140 is that of Holleman.

The printing, unfortunately, is somewhat uneven and frequently out of alignment. A few printer's and other errors have been noticed, but the text is, for a first edition, remarkably free from errata. Without doubt, the book will prove a most serviceable one to those whose first year's laboratory teaching in chemistry requires a text of this character.

ALAN W. C. MENZIES.

Electrical Nature of Matter and Radioactivity. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Second Edition, Completely Revised. New York: D. Van Nostrand Co., 1910. viii + 210 pp. Price, $2.00.

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As Professor Jones aptly states in the preface to the new edition, "Most of the epoch-making discoveries in connection with radioactivity were made in the earlier stages of the work, but many important contributions to our knowledge in this field have been published in the last few years." The first edition of this book was published in 1906 (review: THIS JOURNAL, 28, 1266). To bring it into accord with the later developments occasional pages of the first six chapters have been altered while later chapters have been rewritten or extensively revized. Among the many interesting and important newer results presented are the discovery of ionium, the long-lived transformation product of uranium and the immediate parent of radium; the counting of the alpha particles of a known amount of active matter, which led to the conclusion that the alpha ray is an atom of helium carrying a double positive charge and the evidence that potassium and rubidium are intrinsically, though faintly, radioactive elements. The book shows some evidence of hasty revision; as, for example, on p. 153, where mesothorium 2 and thorium D are omitted from the complete list of thorium products. In this table the periods of mesothorium and thorium A are given as 7 years and 10.6 seconds respectively instead of $5^1/_2$ years and 10.6 hours. The incorrect statements to which attention was called in the review of the first edition have not been changed.

HERBERT N. MCCOY.

Leçons de Cristallographie. G. FRIEDEL. Paris: Librairie Scientifique, A. Hermann et Fils. 1911. 310 pp., 383 figs.

This book was written as a text-book for engineering students and not as a scientific treatise. It presents, in a somewhat extended form, the first lectures in mineralogy given by the author at the National School of Mines at Saint-Etienne, France. Notwithstanding its somewhat elementary character the book offers many interesting thoughts to an advanced crystallographer, but being written in French it is not adapted to English-speaking students. The introduction (pages 1 to 6) discusses the definition of matter whose properties are scalar or vectorial (continuous or discontinuous). Crystallized matter is that which has discontinuous vectorial properties. Under the heading homogeneity a crystal is defined as the entire homogeneous mass of crystallized matter. The first of the two parts of the book is concerned with *the study of the crystal* including geometrical crystallography (pp. 7–125) and physical crystallography (pp. 126–223). The second part of the volume considers *the complex crystallin structures and their transformations*, dealing with twinning, mechanical deformations, liquid crystals, regular and irregular groupings (pp. 225–273), isomorphism (pp. 274–285) and polymorphism (pp. 286–298). A 7-page appendix contains remarks on the structure theory of Schönflies.

WALDEMAR T. SCHALLER.

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Tables for the Determination of Minerals by means of their Physical Properties, Occurrences, and Associates. EDWARD HENRY KRAUS AND WALTER FRED HUNT, 1911. McGraw-Hill Book Company, New York. 254 pp. Price, $2.00 net.

This excellent manual for the "determination of minerals at sight" includes "250 of the most common minerals, classified [by display type] into three groups, which may be designated as (1) very common, (2) common, and (3) not common, but important." The physical properties are described in the introduction and a glossary defines all the terms used in the introduction and in the tables.

The minerals are divided into two groups, according to luster (metallic and non-metallic). The second subdivision is by color, each of which (except for the colorless class) is separated into two smaller sub-divisions on the basis of the streak. The last division is by hardness under which the minerals are separated according to a hardness of calcite or less (1 to 3), harder than calcite but not harder than feldspar (3 to 6), and harder than feldspar (over 6).

To allow for the different phases some minerals show one finds the same mineral placed under several different headings. For example, hornblende, augite, siderite, biotite, garnet, etc., are given under the metallic mineral (with the description of their luster as submetallic or metalloidal) as well as under the non-metallic. Included with minerals are ozocerite' lignite, asphalt, bituminous coal and anthracite coal, given under both metallic and non-metallic luster.

An excellent feature of the tables is that under the individual mineral names is given the page reference to three books (Kraus, "Descriptive Mineralogy" (1911); Dana, "Textbook of Mineralogy" (1898); Moses and Parsons, "Mineralogy" (1909)) where more detailed descriptions of the minerals can be found.

The book is well printed and carefully compiled and should prove of much value to students in the study of minerals by their physical properties.

WALDEMAR T. SCHALLER.

Qualitative Chemical Analysis. By J. I. D. HINDS, Professor of Chemistry, University of Nashville. Easton, Pa.: Chemical Publishing Company, 1910. vii + 265 pp. Price, $2.00.

This volume includes under five parts the following heads: I. Principles and Methods; II. Basic Analysis; III. Acidic Analysis; IV. Complete Analysis of an Unknown; V. Reagents and Tables. The last two are very well arranged. Part III, or Acid Analysis (73 pp.), is based upon Boettger's classification for acids but, according to the author, "the systematic method for their separation and identification is a new arrangement." The laboratory methods in Part II (109 pp.) are those of older texts carefully brought to accord with modern ideas. Part I (49 pp.) introduces a comprehensive discussion of the principles involved in

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qualitative analysis. The connection, however, between this part and the main work—or the actual laboratory methods—is exceedingly weak, with the consequence that Part I stands entirely aloof from the text proper. Theoretical considerations brought into Part II, and often highly involved by reason of a discontinuity of treatment in Part I, must suffer from a pedagogical standpoint. One or two structural formulas are attempted for which experimental evidence up to the present day is entirely lacking. Very few typographical errors are to be found, but the manner of writing certain formulas, such as the hydroxides, if not overlooked in proof-reading, is far from scientific from the standpoint of clearness. Ammonium hydroxide, fortunately, receives a true hydroxide formula in most cases. The action of ammonium sulfide on ferric salts is given on p. 102 as that of a reduction followed by precipitation of ferrous sulfide. This is not in accord with the recent work of Stokes (THIS JOURNAL, **29**, 304). Altogether the text is well put up and the essential features clearly brought out. The introduction of cross references would add much to its serviceability as a laboratory guide. WILLIAM J. HALE.

A Course in Qualitative Chemical Analysis. By CHARLES BASKERVILLE and LOUIS J. CURTMAN. 14 × 22 cm. pp. xi+200. New York: The Macmillan Co., 1910.

The relation of qualitative to quantitative analysis has been emphasized in a way eminently practicable and highly commendable. Terse and somewhat didactic descriptions of reactions furnish a good groundwork for a well arranged system of analysis for the commoner metals and acids. By means of excellent explanatory notes the difficulties met with in an analysis are pointed out, and adjustments of procedure are made apparent.

There are relatively few typographical errors. Minor inconsistencies are evident in the table for preliminary examination, the treatment of alloys and the table of solubilities, where reference is made to a few of the rarer metals and certain less common organic acids. The "Fresenius" table of solubilities leaves much to be desired.

Theoretical explanations are left entirely to the discretion of the instructor. This total lack of theoretical explanations will restrict the general usefulness of the book. For the majority of students throughout the entire country who are pursuing courses in chemistry, qualitative analysis serves chiefly as a complement to the beginning courses in general chemistry. A book which makes qualitative analysis solely the precursor of quantitative analysis, lacks balance. WILLIAM GABB SMEATON.

Alembic Club Reprints No. 18. Sketch of a Course of Chemical Philosophy. By STANISLAO CANNIZZARO (1858). Edinburgh: The Alembic Club. Chicago: The University of Chicago Press, 1911. Price, 43 cents, postpaid.

The Alembic Club Reprints are intended to supply for English the same place as Ostwald's Klassiker der exakten Wissenschaften for German.

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This outline of a course of lectures delived by Cannizzaro at the University of Geneva and published in *Il Nuovo Cimento*, **7**, 321–66 (1858) is an especially happy selection for such a purpose. These lectures contributed very effectively toward the acceptance of Avogadro's Law, and every chemist will find profit in reading them. W. A. N.

Die direkte Einführung von Substituenten in den Benzolkern. By DR. A. F. HOLLEMAN, Professor of Chemistry at the University of Amsterdam. Leipzig: Veit and Co. 516 pp. Price, 20 Marks.

This book by Prof. Holleman is, first of all, a compilation of the scattered data on the subject of direct substitution in the benzene series. The subject is covered through the trisubstituted derivatives. The first section deals with mono-substituted derivatives, the second with the methods available for the quantitative determination of the amounts of each constituent in a mixture of isomers, the third with the introduction of a second substituent into the benzene ring, and the last with the introduction of a third substituent. Several chapters are given to résumés of the facts and general discussions of the theories concerning substitution. In these chapters Prof. Holleman is at his best, for his criticisms of the rules and theories of substitution are exceedingly clear and just. His conclusion that our knowledge of the facts of substitution in the benzene series is still too fragmentary to serve as the basis of any satisfactory theory of substitution is perfectly clear after a study of the book.

As a compilation of facts and literature references the work is a valuable addition to the literature of the benzene series. If this were all the book contained it would be only a reference work, to be used as the need for some definit fact arose, but there are portions of the book which are very readable and which have, therefore, considerable pedagogical value. The chapters on "The Quantitative Determination of Isomers in the Presence of Each Other," and on "The Theories of Substitution" are two chapters of this sort. As a teacher of organic chemistry the reviewer welcomes every book of this type which appears. There is a point in the development of students, just as they are beginning to go beyond the limits of ordinary text-books, when the literature of organic chemistry seems appalling in its complexity. To get hold of a book at this stage which takes some definit thread from the tangled mass and straightens it out is a great relief both for teacher and pupil. Chapters in Prof. Holleman's book will serve admirably this purpose. These chapters are so closely connected with the others, which deal with the great accumulation of facts on the subject of substitution, that they are not apt to give the student a false feeling of mastery of the entire subject when he has read them. The reviewer can heartily recommend Prof. Holleman's work, both as a conveniently and systematically compiled reference book, and as a valuable book for advanced students to read

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in part, when they are making a detailed study of the benzene series.

L. H. CONE.

V. v. Richter. Traité de chimie organique. Par R. ANSCHÜTZ et G. SCHROETER. Premiere édition francaise. Tráduite d'apres la onzième édition allemande par R. GAULT, Tome premier. Série acyclique. Paris: Beranger; 1910. pp. xxiv + 884.

It seems rather surprizing that a French translation of this well known and very successful text-book has been so long in making its appearance. The third American edition, by Professor (now Provost) Edgar F. Smith, was published eleven years ago. This French edition is commended to the translator's compatriots in an introduction by Professor Haller. The book is in attractive form, with good presswork and careful proof-reading, and should be welcomed by all French chemists.

MARSTON TAYLOR BOGERT.

Die Beziehungen zwischen Farbe und Konstitution bei organischen Verbindungen Unter Berücksichtigung der Untersuchungsmethoden. By DR. H. LEY, a. o. Professor an der Universität Leipzig. s. viii + 246. mit 51 Figuren im Text. und 2 Tafeln. Leipzig: Verlag von S. Hirzel, 1911. Price, 8 Marks, bound.

In this book the author discusses the subject of color in organic compounds as related to their chemical constitution. The subject matter has in part appeared in recent volumes of the *Zeitschrift für angewandte Chemie* and the *Jahrbuch für Radioaktivität und Elektronik*, and has been used in the author's lectures at the University of Leipzig.

If one stops to consider, one finds that the very rapid development of organic chemistry as a pure science, and the great interest taken in it during the latter half of the last century, were due more to the scientific investigations of the structure of the dyes, by Hofmann, Baeyer, Fischer and others than to all other causes combined. When we further consider the present vast commercial value of the artificial dye industry, and the great mass of literature on the subject, we must welcome any successful attempt to collect and arrange the most typical examples of color formation; the re ation of the atomic groups to color production; and the working out of theories to account for this phenomenon in a rational manner, and in accordance with our modern ideas of light and atomic structure. This the author has undertaken to do and has within a small compass presented clearly and concisely our present knowledge of the subject, and given many suggestions for further practical studies.

The book is in two parts: In the first part the author discusses color as determined by the absorption spectrum of the compound, and the physical conditions which modify the latter. The chromophore and auxochrome theories, old and new, as modified by our changing idea of valence and atomic structure, are reviewed and developed.

In Chapter VII absorption phenomena are considered from the physical

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rather than the chemical standpoint. A satisfactory explanation of color must rest on phenomena which are intra- or inter-atomic, and be applicable to all colored substances, inorganic as well as organic. It must tell us *why* some simple metallic salts are colored, as well as, for instance, the more complex phenolphthalein salts. The author favors Starks' theory of the electronic structure of atoms, and uses it to explain the color effects which accompany the introduction of the chromophore and auxochrome groups in the molecule. The phenomena of fluorescence are likewise referred to electronic disturbances within the atoms of the compound, thereby affecting the absorption spectrum.

While Baly and Desch's theory of color, as due to "Isorropesis," serves to explain the faint color of some simple compounds, it fails in others, as the metal salts, and methyl iodide, which show selective absorption.

Most cases of color are explained by the author by assuming that the electron, in its electromagnetic field, is the center of color emission within the molecule of the colored compounds.

In the chapter on Color Changes Conditioned by Molecular Rearrangements in Chemical Structure, one finds discussed the work of Hantzsch and others, on the chromoisomers of nitrophenols, nitroketones, nitroaldehydes, aminoazobenzene and triphenylmethane derivatives, and a discussion of the theory of indicators.

A short chapter is devoted to colored "inner complex" salts, utilizing Werner's valence theories to explain the color-formation.

In the perusal of the literature on this subject of color, one can not fail to note the inadequacy of our present structural formulas for showing the delicately balanced inter-relations of the atoms, and the electromagnetic changes which must be continually operative within the molecule of the simplest colored substances.

The second part of this work is devoted to a description of the spectroscopic apparatus and method of studying color phenomena and color changes in the laboratory. It is apparent that spectroscopic methods are rapidly gaining in value, as a practical means of determining structure in organic compounds.

The book is a valuable résumé of our present knowledge of color as related to the structure of organic compounds, and the application of modern ideas of valence and the electronic structure of atoms as a cause of color. It contains many references to the original literature, and should be on the shelves of every chemical library. RICHARD SYDNEY CURTISS.

Practical Physiological Chemistry. By PHILIP B. HAWK, M.S., Ph.D. Third Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son and Co., 1910. Price, $2.50.

A third edition following so soon after the second is sufficient to show the favor with which this very useful book has been received. The

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new edition differs from the second, reviewed in THIS JOURNAL, 31, 607 (1909), by certain corrections and by the addition of some new quantitative matter. This is a decided improvement since a quantitative experiment teaches, as a rule, much more than a qualitative one. The many admirable features of the work and its main defects have been mentioned in the former review. The reviewer uses this work in teaching his classes but finds it advizable to require a good deal more quantitative work and also the isolation, in a fairly pure state, of several physiologically important substances. ALBERT P. MATHEWS.

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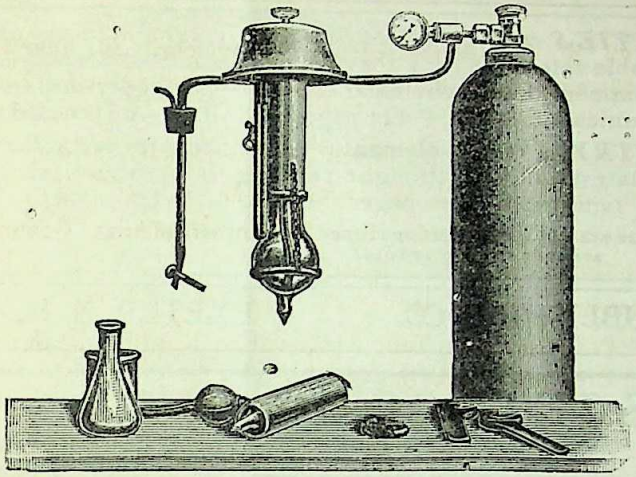
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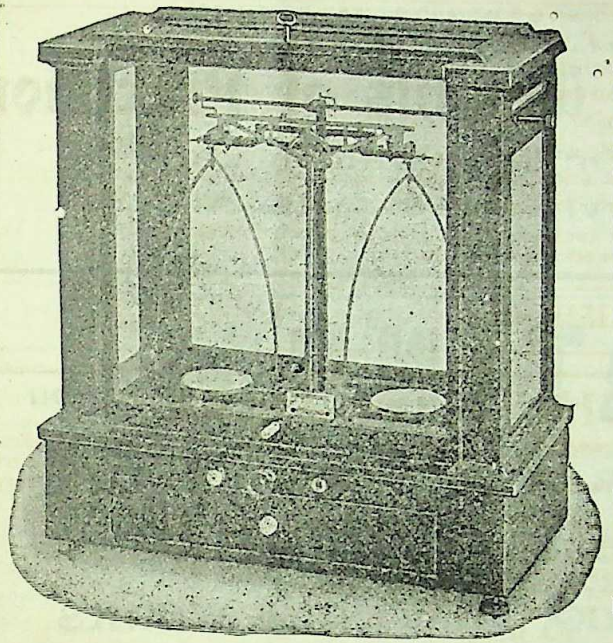
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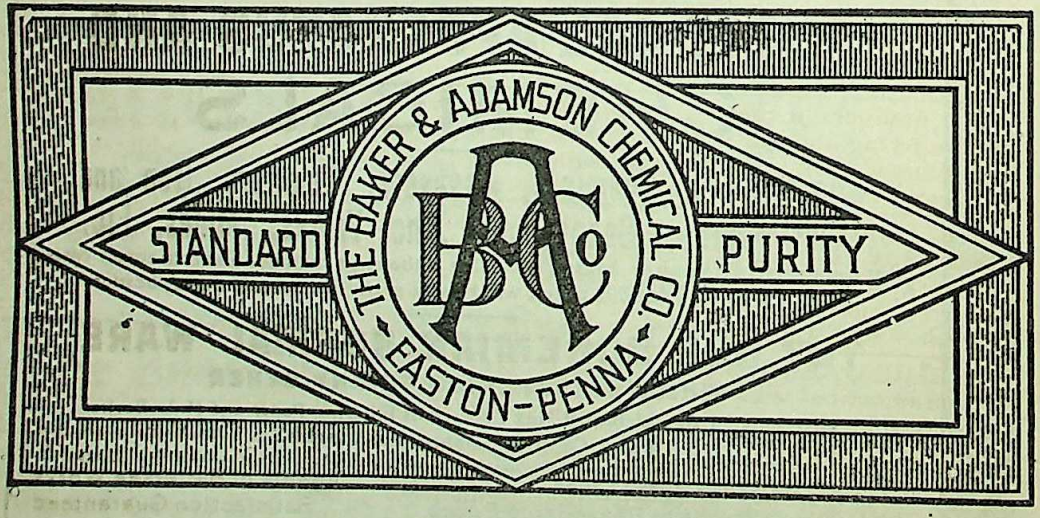
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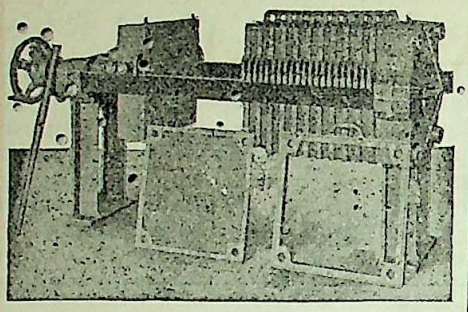
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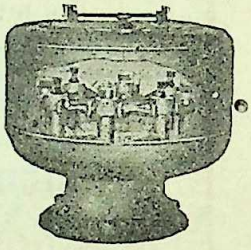


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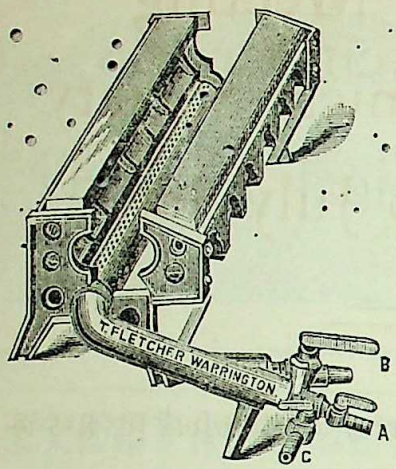
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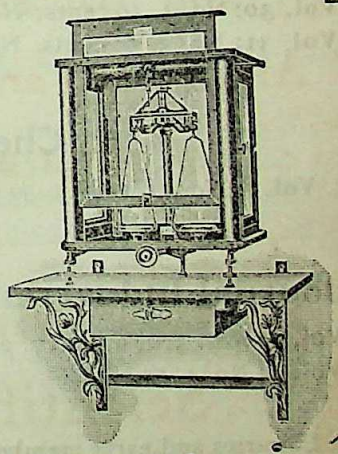
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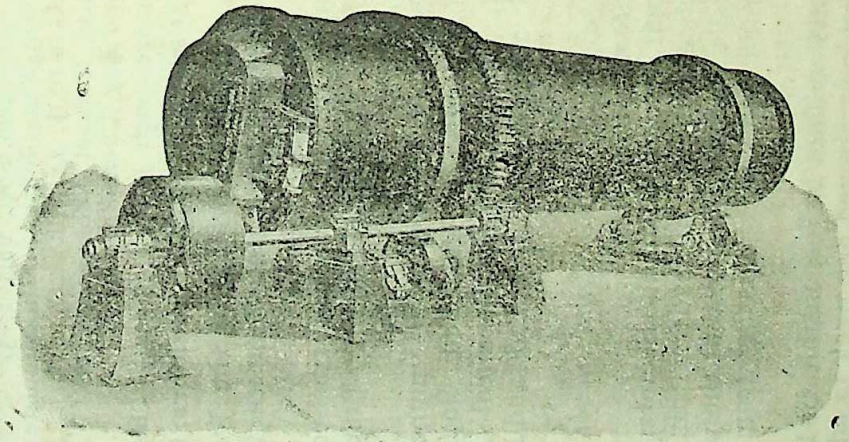
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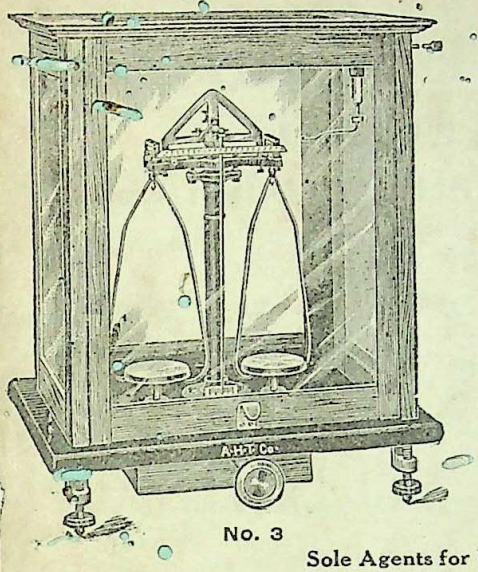
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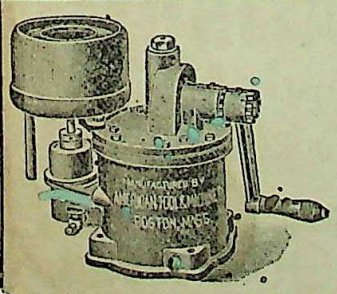
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